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ELIMINATION OF THE NITRILE GROUP FROM *o*-AMINONITRILES—IV[1]

A NEW AND EFFICIENT SYNTHESIS OF 3,5-DIARYLAMINOBENZENES FROM ARYLIDENEMALONODINITRILES AND 1-ARYLETHYLIDENEMALONODINITRILES

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Abstract—A synthesis of a variety of 5'-amino-*m*-terphenyls (**6**) and 3,5-diarylaminobenzenes through an efficient elimination of cyano groups from 5'-amino-4',6'-dicyano-*m*-terphenyls (**4**) using sodium hydroxide in ethanol at 220°, is described, The starting *o*-aminonitriles (**4**) are conveniently prepared from arylidenemalonodinitriles (**1**) and 1-arylethylidenemalonodinitriles (**2**). This strategy is applied for the synthesis of an aminoquaterphenyl (**13**) and a diaminoquinquephenyl (**16**).

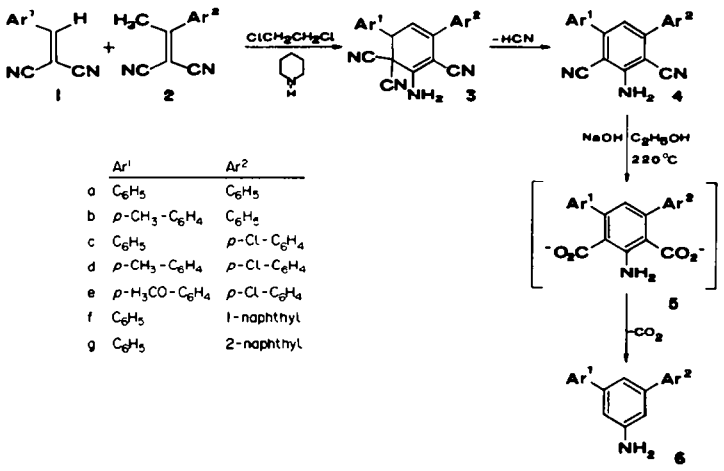
The synthesis and chemistry of 1,3-diarylbenzenes has been extensively investigated. A variety of synthetic routes to these hydrocarbons has been reported. The central ring of *m*-diarylbenzenes is constructed from appropriate precursors furnishing a carbocyclic 6-membered ring which is then aromatized in two or three steps. The reactions of chalcones with carbonyl compounds affords 3,5-diaryl-2-cyclohexen-1-ones, the key ketone in a synthetic approach known as the "chalcone route".[2–8] The dehydration and dehydrogenation of this ketone leads to the desired hydrocarbon. 3 - Ethoxy - 2 - cyclohexen - 1 - one is also a valuable reagent for the synthesis of *m*-diarylbenzenes via an "enol ether route".[8,9–15] This compound is treated with aryllithium or Grignard reagents and the resulting arylcyclohexenone is further reacted with these reagents affording diarylcyclohexenones. They are converted into hydrocarbons in the dehydration and aromatization steps. The central ring of *m*-diarylbenzenes has been synthesized recently by the intramolecular cyclization involving unsaturated aldehydes.[16] An alternative synthetic approach involves the reductive phenylation of nitroarenes[17] or is based on the Ullmann reaction of aryl iodides.[18] The *m*-diarylbenzenes can be constructed from suitable aryl iodides and this route has been recently extensively exploited.[19,20]

RESULTS AND DISCUSSION

The base catalyzed dimerization of ylidenemalonodinitriles synthesized from a variety of ketones leads to substituted cyclohexadiene derivatives.[21,22] This very easily accessible class of compounds has found, however, only limited synthetic applications mostly due to difficulties in aromatization of the carbocyclic 6-membered ring. A modification of the dimerization reaction involves the interaction of arylidenemalonodinitriles (**1**) and 1-arylethylidenemalonodinitriles (**2**) leading to diarylcyclohexadiene derivatives (**3**), which may be described as "mixed dimers" (Scheme 1). In contrast with typical ylidenemalonodinitrile dimers, the cyclohexadiene derivatives thus obtained are prone to aromatization by elimination of hydrogen cyanide. In some instances the driving force of aromatization is so enhanced that the intermediate diaryl cyclohexadiene derivatives (**3**) cannot be isolated and the reaction affords only diaryl *o*-aminonitriles (**4**). The synthesis of *o*-aminonitriles (**4**) has been investigated by Gewald,[23] and Sharanin *et al.*[24] However, to our knowledge these readily available compounds have not found any synthetic application presumably due to high resistance of the cyano groups of **4** to hydrolysis or other synthetic transformations. This very convenient synthesis of diaryl *o*-aminonitriles (**4**) attracted our attention as a potential useful route to amino derivatives of *m*-terphenyls and of other 3,5-diarylaminobenzenes. The advantage of the synthetic approach presented here is the formation of a central aromatic ring of *m*-diarylbenzene system in a single step from easily accessible precursors **1** and **2**.

The Michael addition of **2** to **1** is followed by intramolecular cyclization furnishing the cyclohexadiene (**3**). In some instances, however, only the *o*-aminonitriles (**4**) are isolated. The reaction is carried out in ethanol, methanol, or diethyl ether and is catalyzed by morpholine, piperidine, and triethylamine. The cyclohexadienes (**3**) can be converted into **4** in a separate step by the elimination of hydrogen cyanide using strong bases.[23,24] The intramolecular cyclization is concurrent with other reactions leading to substituted 1,3-butadienes.[24] The elimination of hydrogen cyanide from **3** also competes with the ring-opening reaction of cyclohexadienes leading to substituted hexatrienes which usually undergo further complex transformations.[25] It was essential for our purposes to maximize yields of aromatic *o*-aminonitriles (**4**) and to suppress the formation of undesired side-products. We needed a simple and convenient one-step preparation of **4** directly from ylidenemalonodinitriles **1** and **2**. Our approach involved the reaction of **1** and **2** in 1,2-dichloroethane, catalyzed by piperidine. For some *o*-aminonitriles the yields were lower than the nearly-quantitative yields reported previously.[23]

Ring closure of some ylidenemalonodinitriles gives rise to a variety of carbocyclic *o*-aminonitriles.[26,27] The cyano group of these compounds is usually very resistant



	Ar¹	Ar²
a	C_6H_5	C_6H_5
b	p-CH_3-C_6H_4	C_6H_5
c	C_6H_5	p-Cl-C_6H_4
d	p-CH_3-C_6H_4	p-Cl-C_6H_4
e	p-H_3CO-C_6H_4	p-Cl-C_6H_4
f	C_6H_5	1-naphthyl
g	C_6H_5	2-naphthyl

Scheme 1.

to hydrolysis or other reactions. We have found that heating of these *o*-aminonitriles in an autoclave in an ethanolic solution of sodium hydroxide causes the elimination of the cyano function and aromatic amines are obtained in good to excellent yields. This approach has opened a new route to aromatic amines which are difficult to synthesize by other methods, and then to parent hydrocarbons.[28–30] As a continuation of our investigation on the application of carbocyclic *o*-aminonitriles for the synthesis of aromatic amines, we have carried out the elimination of both cyano groups from a variety of diaryl *o*-aminonitriles (**4**). Heating of **4** in ethanolic sodium hydroxide in an autoclave at 220° for several hours resulted in the isolation of 3,5-diarylaminobenzenes (**6**) in moderate to good yields. This one-step synthesis of **6** from **4** proceeds presumably via decarboxylation of intermediate products of hydrolysis (**5**). The hydrolysis and decarboxylation of **4** seems to be facilitated by severe reaction conditions. We observed earlier that under similar reaction conditions, some carbocyclic *o*-amino-amides gave aromatic amines via elimination of the carbamoyl group.[30]

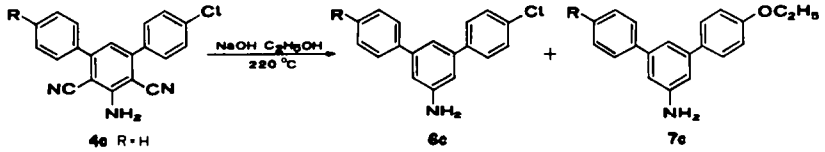
The aromatic amines (**6**) are remarkably stable under these elimination conditions. However, the application of our synthetic strategy appears to be limited to *o*-aminonitriles (**4**) which do not have base-sensitive groups in the side rings. The amine (**6a**) has been prepared previously by aromatization of 3,5-diphenyl-2-cyclohexenone oxime[4] or from 3,5-diiodo-1-nitrobenzene via the Ullmann reaction.[19] All other aromatic amines reported here are new compounds.

Dicyano-amino-terphenyls (**4**) having Cl atoms in the side rings are also easily synthesized from ylidenemalonodinitriles.[24] It was of interest to investigate the elimination of the cyano groups from **4c**, **4d**, and **4e** for the purpose of discovering whether the Cl atom would be replaced by a nucleophilic group under the elimination conditions. The ^{1}H-NMR spectra of obtained amines **6c**, **6d**, and **6e** revealed also the presence of products **7c**, **7d**, and **7e** resulting from the substitution of the Cl atom by the OEt group (Scheme 2). The OEt group of **7c** appeared in the NMR spectrum as a quartet at δ 4.11 and as a triplet at δ 1.42. Attempts to obtain analytically pure samples of **6c**, **6d**, and **6e** by TLC separation of **7** or by several recrystallizations were unsuccessful. As estimated from the NMR spectra, the amount of **7c**, **7d**, and **7e** in **6c**, **6d**, and **6e**, respectively, did not exceed 10%.

The reaction of **1a** and **8** afforded the *o*-aminonitrile (**9**)[23] which then gave the amine **10** in 45% yield (Scheme 3). In this manner an alkyl group may be introduced into the 2′ position of the *m*-terphenyl system. Our attempt to synthesize the *m*-terphenyl derivative having the phenyl group at the 2′ position was unsuccessful. The reaction of an ylidenemalonodinitrile obtained from desoxybenzoin[31] and **1a** did not lead to the expected dicyanotriphenylaniline.

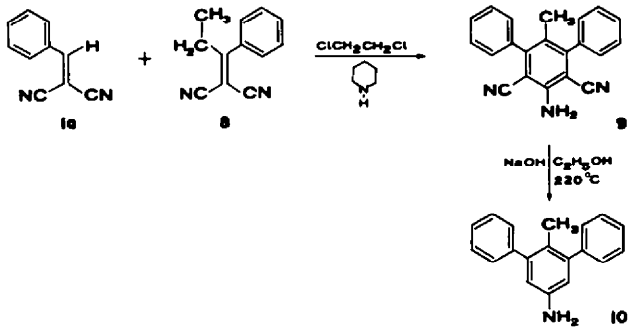
The convenient synthesis in two steps of 5′-amino-*m*-terphenyls from ylidenemalonodinitriles prompted us to investigate the application of this synthetic approach for the construction of some polyphenyl systems (Scheme 4).

The reaction of ylidenemalonodinitrile (**11**) and **1a** gave the substituted quaterphenyl (**12**) which was then converted into **13** in 23% yield. The reaction of **14** and **2a** involved formation of two new armatic rings of the substituted quinquephenyl (**15**) in one synthetic step. The elimination of four cyano groups from **15** under the

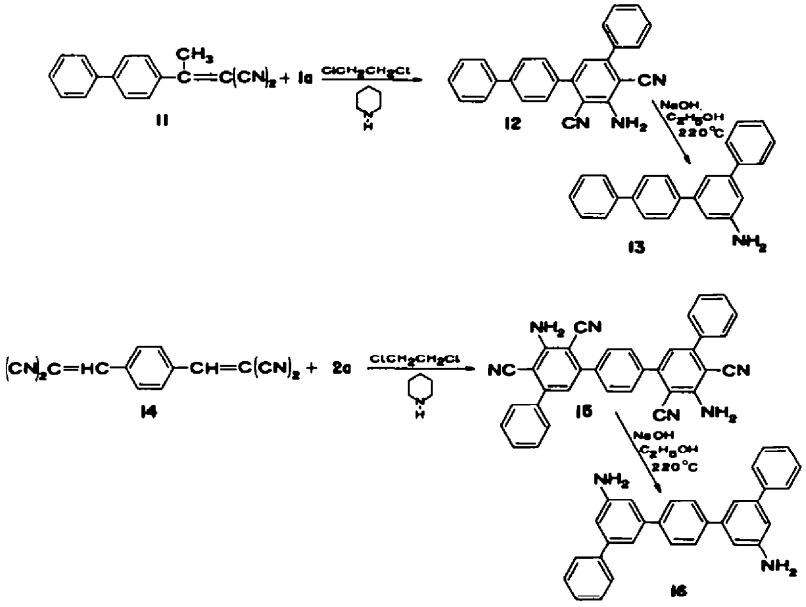


4c R = H **6c** **7c**
4d R = CH_3 **6d** **7d**
4e R = H_3CO **6e** **7e**

Scheme 2.



Scheme 3.



Scheme 4.

usual conditions afforded the diamine (**16**). The starting nitrile (**14**) was simply prepared from terephthalaldehyde.[32] The elimination reactions reported here offer in fact the proof of structure of the *o*-aminonitriles (**4**). The UV spectra of the amines (**6**) are consistent with earlier reported data for **6a**[5] and the *m*-terphenyl system.[33] The IR spectra of **6** show a typical amino-group absorption in the 3300–3400 cm^{-1} region. The aromatic proton resonances of **6** usually appear in ^{1}H-NMR spectra as a complex multiplet. Two protons in the ortho positions with respect to the amino group are shielded and appear 0.2–0.3 ppm upfield. The resonances of the two phenyl rings of the amine (**10**) appear as a relatively narrow singlet at δ 7.45. This reflects specific arrangement in the space of phenyl rings of the amine (**10**) due to the presence of the Me group in the 2′ position of **10**. The mass spectra of all amines show very intense molecular ion peaks.

The elimination of the cyano groups from *o*-aminonitriles (**4**) is facilitated by the amino function. In order to investigate the scope of this elimination reaction, we attempted to decyanate the hindered nitrile (**17**)[34] under usual conditions (Scheme 5).

Scheme 5.

Heating of **17** in ethanolic solution of sodium hydroxide in an autoclave for several hours caused only the hydrolysis of the nitrile group. The amide (**18**) crystallized out from the reaction mixture and was isolated in 80% yield. Careful work-up of the basic solution did not afford any traces of a carboxylic acid or a parent hydrocarbon.

The present synthetic strategy for the construction of polyphenyl systems having *m*-substituted benzene units has some advantages. The starting 1-arylethylidenemalonodinitriles (**2**) are obtained from aryl methyl ketones, which are easily synthesized from aromatic hydrocarbons by many synthetic routes. Arylidenemalonodinitriles (**1**) are very easily obtained

from a variety of aromatic aldehydes. The reaction of **1** and **2** is essentially a one-pot synthesis which involves the formation of a new aromatic ring. The elimination of the cyano functions from polyphenyl derivatives affords in one step aromatic amines.

EXPERIMENTAL

M.ps are uncorrected. Elemental analyses were performed by the Regional Laboratory of Physico-Chemical Analyses, Krakow. The UV spectra were recorded on a Specord UV/VIS (Carl Zeiss, Jena) spectrometer and IR spectra were obtained on a UR-10 (Carl Zeiss, Jena) spectrometer. The ^{1}H-NMR spectra were recorded on a Varian (100 MHz) spectrometer using Me_4Si as internal standard. The mass spectra were obtained on a LKB-9000 S instrument at 70 eV ionizing energy.

Preparation of starting ylidenemalonodinitriles

Arylidenemalonodinitriles (**1**) were obtained by condensation of equimolar amounts of aromatic aldehydes and malonodinitrile in EtOH, catalyzed by a few drops of piperidine.[35] The physical and spectral data for obtained products were in good agreement with the reported data for **1a**,[36] **1b**,[37] **1e**,[38] and **14**.[32] Compounds **2** were obtained by condensation of aryl methyl ketones and malonodinitrile under conditions described.[39] Their physical and spectral properties were in agreement with the published data for **2a**,[39] **2c**,[39] **2f**,[40] **2g**,[41] and **8**.[36]

1-(*4-Biphenyl*)*ethylidenemalonodinitrile* (**11**)

The condensation of 4-acetylbiphenyl (16.0 g, 0.08 mol) with malonodinitrile (5.5 g, 0.08 mol) was performed under conditions reported.[39] Recrystallization of the product from EtOH gave 12.5 g (63%) of **11** as yellowish needles, m.p. 164–165°. IR (nujol) cm^{-1} 2215 (C≡N). (Found: C, 83.40; H, 4.99; N, 11.26. Calc for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47%.)

The synthesis of 1-*amino*-2,6-*dicyano*-3,5-*diarylbenzenes* (**4**)

General procedure. Equimolar amounts of **1** and **2** (20 mmol) were suspended in 1,2-dichloroethane (30 ml) and piperidine (2.0 ml) was slowly added to the magnetically stirred suspension. Usually the addition of the first drops of piperidine caused the separation of a ppt and warming-up of the mixture. The resulting slurry was stirred for 30 min without external heating and then was refluxed and stirred for 1.5–2 hr. Heating of the mixture was accompanied by the evolution of HCN. The ppt was filtered off, washed with EtOH and recrystallized from appropriate solvent. The *o*-aminonitriles (**4**) are sparringly soluble in most common solvents. These compounds sublime under reduced pressure and, if necessary, can be also purified by sublimation. Compounds (**4**) especially **4f**, **4g**, and **12** show moderate fluorescence in dilute solns in EtOH or acetone. The IR and ^{1}H-NMR spectra of **4a**, **4b**, **4c**, and **9** were reported previously[23,24] and are in agreement with our spectral data for these compounds.

5′-*Amino*-1,1′:3′,1″-*terphenyl*-4′,6′-*dicarbonitrile* (**4a**). Yield 62%, m.p. 226° (from EtOH), lit.[23] m.p. 226°.

5′-*Amino*-4-*methyl*-1,1′:3′,1″-*terphenyl*-4′,6′-*dicarbonitrile* (**4b**). Yield 56%, m.p. 208° (from EtOH), lit.[24] m.p. 207°.

5′-*Amino*-4-*chloro*-1,1′:3′,1″-*terphenyl*-4′,6′-*dicarbonitrile* (**4c**). Yield 77%, m.p. 253–254° (from nitromethane), lit.[24] m.p. 250–251°.

5′-*Amino*-4-*chloro*-4″-*methyl*-1,1′:3′,1″-*terphenyl*-4′,6′-*dicarbonitrile* (**4d**). Yield 44%, m.p. 285–286° (from nitromethane); IR (nujol) cm^{-1} 3481, 3374, 3255 (NH_2), 2223, 2210 (CN), 1647, 1100, 822. (Found: C, 73.27; H, 4.07; N, 12.20. Calc for $C_{21}H_{14}ClN_3$: C, 73.36; H, 4.10; N, 12.22%.)

5′-*Amino*-4-*chloro*-4″-*methoxy*-1,1′:3′,1″-*terphenyl*-4′,6′-*dicarbonitrile* (**4e**). Yield 24%, m.p. 257° (from ethanol); IR (nujol) cm^{-1} 3488, 3383, 3250 (NH_2), 2220 (CN), 1645, 1187, 1100, 1038, 830. (Found: C, 69.81; H, 3.90; N, 11.45. Calc for $C_{21}H_{14}ClN_3O$: C, 70.10; H, 3.92; N, 11.68%.)

3-*Amino*-5-(1-*naphthyl*)*biphenyl*-2,4-*dicarbonitrile* (**4f**). Yield 43%, m.p. 188° (from ethanol); IR (nujol) cm^{-1} 3497, 3388, 3249 (NH_2), 2218 (CN), 1635, 1577, 1553, 862, 823, 770, 757, 706. (Found: C, 83.54; H, 4.44; N, 11.95. Calc for $C_{24}H_{15}N_3$: C, 83.46; H, 4.38; N, 12.16%.)

3-*Amino*-5-(2-*naphthyl*)*biphenyl*-2,4-*dicarbonitrile* (**4g**). Yield 32%, m.p. 187° (from ethanol); IR (nujol) cm^{-1} 3500, 3402, 3253 (NH_2), 2218 (CN), 1633, 1578, 860, 705. (Found: C, 83.62; H, 4.40; N, 12.12. Calc for $C_{24}H_{15}N_3$: C, 83.46; H, 4.38; N, 12.16%.)

5′-*Amino*-2′-*methyl*-1,1′:3′,1″-*terphenyl*-4′,6′-*dicarbonitrile* (**9**). Yield 32%, m.p. 229–231° (from ethanol), lit.[23] m.p. 229–231°.

5′-*Amino*-1,1′:3′,1″:4″,1‴-*quaterphenyl*-4′,6′-*dicarbonitrile* (**12**). Yield 44%, m.p. 228° (from ethanol); IR (nujol) cm^{-1} 3470, 3365, 3233 (NH_2), 2220 (CN), 1623, 1567, 778, 765, 703. (Found: C, 83.95; H, 4.46; N, 11.27. Calc for $C_{26}H_{17}N_3$: C, 84.07; H, 4.61; N, 11.31%.)

5′,5‴-*Diamino*-1,1′:3′,1″:4″,1‴:3‴,1⁗-*quinquephenyl*-4′,6′,4‴,6‴-*tetracarbonitrile* (**15**). The reaction of **14**[32] (3.0 g, 13 mmol) with **2a** (4.4 g, 26 mmol) was catalyzed by piperidine (1.0 ml) and was carried out in usual manner in ethylene chloride (30 ml). Crude product was filtered off, washed with ethylene chloride and ethanol, and recrystallized from nitromethane to afford 2.3 g (34%) of **15**, m.p. 361°; IR (nujol) cm^{-1} 3490, 3370, 3256 (NH_2), 2220 (CN), 1640, 1580, 1556, 1292, 833, 769, 704. (Found: C, 79.23; H, 4.02; N, 16.14. Calc for $C_{34}H_{20}N_6$ (512.6): C, 79.67; H, 3.93; N, 16.39%.)

Elimination of the nitrile groups from o-aminonitriles **4**, **9**

General procedure. An *o*-aminonitrile (4 mmol, unless otherwise stated) was suspended in a soln of NaOH (1.5 g) in EtOH (60 ml). The mixture was placed in a Ni-vessel and was heated at 220° for 5 hr in a 250 ml autoclave. The opening of the autoclave was accompanied by the evolution of some amount of ammonia. EtOH was evaporated and the residue was mixed with water and the solid was filtered by suction. The crude amine was purified by sublimation *in vacuo* and then by recrystallization from appropriate solvent.

5′-*Amino*-1,1′:3′,1″-*terphenyl* (**6a**). Yield 911 mg (93%), colorless crystals from cyclohexane, m.p. 110.5°, lit.[4] m.p. 109–110°; UV λ_{max}^{MeOH} nm (ε): 247 (36,000), 321 (3000); IR (KBr) cm^{-1} 3452, 3374 (NH_2), 1618, 1598, 1577, 872, 863, 772, 711; ^{1}H-NMR ($CDCl_3$) δ, ppm 7.63–7.07 (m, 11H, Ar—H), 6.80 (s, 2H, Ar—H), 3.67 (s, 2H, NH_2); MS *m/z* (rel. int.) 246 (21), 245 (M^+, 100), 244 (9), 243 (8), 215 (5), 115 (7).

5′-*Amino*-4-*methyl*-1,1′:3′,1″-*terphenyl* (**6b**). Yield 973 mg (94%), colorless small needles from n-hexane–benzene (3:1), m.p. 105°; UV λ_{max}^{MeOH} nm (ε): 250 (29,700), 322 (3300); IR (KBr) cm^{-1} 3438, 3311, 3213 (NH_2), 1622, 1603, 1578, 870, 828, 772, 709; ^{1}H-NMR ($CDCl_3$) δ, ppm 7.75–7.26 (m, 10H, Ar—H), 6.92 (s, 2H, Ar—H), 3.75 (s, 2H, NH_2), 2.41 (s, 3H, CH_3); MS *m/z* (rel. int.) 260 (21), 259 (M^+, 100), 258 (8), 243 (6), 129 (6). (Found: C, 88.11; H, 6.50; N, 5.16. Calc for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40%.)

The decyanation of **4c**. The suspension of **4c** (1.320 g, 4 mmol) was heated in ethanolic NaOH soln (2.0 g of NaOH, 60 ml of EtOH) in an autoclave at 220° for 5 hr. The solid product was sublimed *in vacuo* and recrystallized from n-hexane–benzene (4:1) to afford 935 mg of the mixture of **6c** and **7c** as colorless small needles, m.p. 95–96°; IR (KBr) cm^{-1} 3436, 3312, 3210 (NH_2); ^{1}H-NMR ($CDCl_3$) δ, ppm **6c** and **7c**: 7.74 (m, Ar—H), 6.94 (s, Ar—H), 3.79 (s, NH_2). The OEt group of **7c** appeared as a quartet at δ 4.11 (J = 7 Hz) and as a triplet at δ 1.42 (J = 7 Hz). The ratio **6c**:**7c** (10:1) was estimated from the integrated peak areas. The separation of **7c** from **6c** by repeated crystallizations or TLC separation was unsuccessful, as shown by ^{1}H-NMR spectra.

The decyanation of **4d**. The suspension of **4d** (1.379 g, 4 mmol) was decyanated at the same conditions as described for **4c**. The solid product was sublimed *in vacuo* and recrystallized from n-hexane–benzene (3:1) to afford 977 mg of the mixture of **6d** and **7d** as colorless needles, m.p. 149°; IR (KBr) cm^{-1} 3438, 3305, 3200 (NH_2); ^{1}H-NMR ($CDCl_3$) δ, ppm **6d** and **7d**: 7.68–

7.21 (m, Ar—H), 6.92 (s, Ar—H), 3.76 (s, NH_2), 2.38 (s, CH_3). The OEt group of **7d** appeared at δ 4.09 (q, J = 7 Hz) and 1.42 (t, J = 7 Hz). The ratio of **6d** : **7d** (9 : 1) was estimated from the NMR spectrum.

The decyanation of **4e**. The suspension of **4e** (546 mg, 1.5 mmol) was heated in an autoclave at 220° for 5 hr in the soln of NaOH (1.0 g) in EtOH (60 ml). The product was sublimed *in vacuo* and recrystallized from cyclohexane to afford 141 mg of the mixture of **6e** and **7e** as colorless small needles, m.p. 127°; IR (KBr) cm^{-1} 3436, 3305, 3200 (NH_2); ^{1}H-NMR ($CDCl_3$) δ, ppm **6e** and **7e**: 7.65–6.99 (m, Ar—H), 6.89 (s, Ar—H), 3.88 (s, OCH_3), 3.84 (s, NH_2). The ethoxy group of **7e** appeared at δ 4.09 (q, J = 7 Hz) and 1.42 (t, J = 7 Hz). The ratio **6e** : **7e** (11 : 1) was estimated from the NMR spectrum.

5-Amino-3-(1-naphthyl)biphenyl (**6f**). Yield 800 mg (68%), colorless fluffy needles from ethanol, m.p. 114°; UV λ_{max}^{MeOH} nm (ε) 225 (34,200), 250 (44,400); IR (KBr) cm^{-1} 3440, 3392, 3311, 3208 (NH_2), 1618, 1600, 861, 832, 772, 760, 709; ^{1}H-NMR ($CDCl_3$) δ, ppm 8.11 (s, 1H, Ar—H), 8.00–7.38 (m, 12H, Ar—H), 7.01 (s, 1H, Ar—H), 6.94 (s, 1H, Ar—H), 3.77 (s, 2H, NH_2); MS *m/z* (rel. int.) 296 (23), 295 (M^+, 100), 294 (7), 148 (9). (Found: C, 89.60; H, 5.68; N, 4.54. Calc for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74%.)

5-Amino-3-(2-naphthyl)biphenyl (**6g**). Yield 820 mg (69%), colorless small needles from EtOH, m.p. 116–117°; UV λ_{max}^{MeOH} nm (ε) 224 (33,000), 250 (44,500); IR (KBr) cm^{-1} 3438, 3305, 3210 (NH_2), 1626, 1600, 1576, 863, 835, 772, 759, 711; ^{1}H-NMR ($CDCl_3$) δ, ppm 8.10 (s, 1H, Ar—H), 7.97–7.36 (m, 12H, Ar—H), 6.98 (s, 1H, Ar—H), 6.90 (s, 1H, Ar—H), 3.71 (s, 2H, NH_2); MS *m/z* (rel. int.) 296 (25), 295 (M^+, 100), 294 (7), 148 (10). (Found: C, 89.46; H, 5.61; N, 4.59. Calc for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74%.)

5'-Amino-2'-methyl-1,1':3',1''-terphenyl (**10**). The decyanation of **9** (1.237 g, 4 mmol) in the usual manner gave 465 mg (45%) of **10** as colorless long needles from n-hexane, m.p. 117–118°; UV λ_{max}^{MeOH} nm (ε): 228 (21,000), 307 (2000); IR (KBr) cm^{-1} 3421, 3350 (NH_2), 1620, 1598, 1578, 1495, 1463, 1437, 876, 789, 760, 713; ^{1}H-NMR ($CDCl_3$) δ, ppm 7.45 (s, 10H, Ar—H), 6.67 (s, 2H, Ar—H), 3.57 (s, 2H, NH_2), 2.00 (s, 3H, CH_3); MS *m/z* (rel. int.) 260 (21), 259 (M^+, 100), 258 (37), 257 (6), 241 (6), 182 (7), 180 (9). (Found: C, 87.97; H, 6.55; N, 5.24. Calc for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40%.)

5' - Amino - 1,1':3',1'':4'',1''' - quaterphenyl (**13**). The decyanation of **12** (945 mg, 2.5 mmol) was carried out in an autoclave in an NaOH soln (1.5 g) in EtOH (60 ml). Sublimation of the product *in vacuo* and recrystallization from cyclohexane gave 189 mg (23%) of **13** as colorless small needles, m.p. 168°; UV λ_{max}^{MeOH} nm (ε): 265 (31,300); IR (KBr) cm^{-1} 3450, 3373 (NH_2), 1617, 1600, 1580, 1283, 847, 785, 708; ^{1}H-NMR ($CDCl_3$) δ, ppm 7.80–7.30 (m, 15H, Ar—H), 6.98 (s, 2H, Ar—H), 3.80 (s, 2H, NH_2); MS *m/z* (rel. int.) 322 (25), 321 (M^+, 100), 161 (9). (Found: C, 89.93; H, 5.89; N, 4.21. Calc for $C_{24}H_{19}N$: C, 89.68; H, 5.96; N, 4.36%.)

5',5''' - Diamino - 1,1':3',1'':4'',1''':3''',1'''' - quinquephenyl (**16**). The suspension of **15** (1.000 g, 2 mmol) was heated in an autoclave in ethanolic NaOH soln (2.0 of NaOH, 60 ml of EtOH) for 5 hr at 220°. The mixture was diluted with water and the ppt was filtered off, washed with water and sublimed under reduced pressure. Recrystallization from EtOH gave 235 mg (29%) of **16** as colorless crystals, m.p. 251°; UV λ_{max}^{MeOH} nm (ε): 262 (36,300); IR (KBr) cm^{-1} 3450, 3373 (NH_2), 1617, 1600, 1224, 871, 862, 844, 776, 712; ^{1}H-NMR (DMSO-d_6) δ, ppm 7.90–7.45 (m, 14H, Ar—H), 7.23 (s, 2H, Ar—H), 7.05 (s, 2H, Ar—H), 7.02 (s, 2H, Ar—H), 5.38 (s, 4H, NH_2); MS *m/z* (rel. int.) 414 (6), 413 (35), 412 (M^+, 100), 411 (6), 206 (9), 167 (4). (Found: C, 87.58; H, 5.74; N, 6.62. Calc for $C_{30}H_{24}N_2$: C, 87.35; H, 5.86; N, 6.79%.)

2' - Carbamoyl - 1,1':3',1'':5',1''' - quaterphenyl (**18**). A suspension of **17**[34] (1.000 g, 3 mmol) in the soln of NaOH (1.5 g) in EtOH (60 ml) was heated in an autoclave at 220° for 5 hr. The precipitated colorless plates were separated from the basic soln by filtration and washed with water. Recrystallization from EtOH gave 843 mg (80%) of **18**, m.p. 244°; IR (nujol) cm^{-1} 3462, 3283, 3168 (NH_2), 1641 (C=O), 772. (Found: C, 85.81; H, 5.37; N, 4.24. Calc for $C_{25}H_{19}NO$: C, 85.93; H, 5.48; N, 4.01%.)

REFERENCES

[1] Part III: J. Sepioł, *Pol. J. Chem.* **53**, 2401 (1979).
[2] D. M. W. Anderson, N. Campbell, D. Leaver and W. H. Stafford, *J. Chem. Soc.* 3992 (1959).
[3] N. B. Sunshine and G. F. Woods, *J. Org. Chem.* **28**, 2517 (1963).
[4] W. Polaczkowa and N. Porowska, *Roczniki Chem.* **34**, 1659 (1960).
[5] W. Polaczkowa, N. Porowska and B. Dybowska, *Ibid.* **36**, 41 (1962).
[6] H. E. Zimmerman, D. F. Juers, J. M. McCall and B. Schröder, *J. Am. Chem. Soc.* **93**, 3662 (1971).
[7] N. Arumugam and A. Kumaraswamy, *Synthesis* 367 (1981).
[8] P. Melzer, H. Kurreck and W. Kieslich, *Chem. Ber.* **115**, 3597 (1982).
[9] G. F. Woods and I. W. Tucker, *J. Am. Chem. Soc.* **70**, 2174, 3340 (1948).
[10] G. F. Woods and F. T. Reed, *Ibid.* **71**, 1348 (1949).
[11] G. F. Woods, F. T. Reed, T. E. Arthur and H. Ezekiel, *Ibid.* **73**, 3854 (1951).
[12] R. L. Alexander, *J. Org. Chem.* **21**, 1464 (1956).
[13] M. Bennett, N. B. Sunshine and G. F. Woods, *Ibid.* **28**, 2514 (1963).
[14] G. F. Woods, D. D. Centola, H. E. Ruskie and C. D. Miller, *J. Am. Chem. Soc.* **82**, 5227 (1960).
[15] H. A. Staab and F. Binnig, *Chem. Ber.* **100**, 293 (1967).
[16] M. A. Tius and S. Savariar, *Synthesis* 467 (1983).
[17] T. Ohta, R. Machida, K. Takeda, Y. Endo, K. Shudo and T. Okamoto, *J. Am. Chem. Soc.* **102**, 6385 (1980).
[18] P. E. Fanta, *Synthesis* 9 (1974).
[19] S. Ozasa, Y. Fujioka, J. Kikutake and E. Ibuki, *Chem. Pharm. Bull.* **31**, 1572 (1983).
[20] S. Ozasa, Y. Fujioka, H. Hashino, N. Kimura and E. Ibuki, *Ibid.* **31**, 2313 (1983).
[21] J. K. Williams, *J. Org. Chem.* **28**, 1054 (1963).
[22] J. J. Baldwin, A. W. Raab and G. S. Ponticello, *Ibid.* **43**, 2529 (1978).
[23] K. Gewald and W. Schill, *J. Pr. Chem.* **313**, 678 (1971).
[24] Yu. A. Sharanin, Yu. A. Baskakov, Yu. T. Abramenko, Yu. G. Putsykin, A. F. Vasilev and E. B. Nazarova, *Zh. Org. Khim.* **16**, 2192 (1980).
[25] Yu. A. Sharanin, Yu. A. Baskakov, Yu. T. Abramenko, Yu. G. Putsykin, E. B. Nazarova and A. F. Vasilev, *Ibid.* **20**, 1508 (1984).
[26] E. Campaigne and S. W. Schneller, *Synthesis* 705 (1976).
[27] A. J. Fatiadi, *Ibid.* 165, 241 (1978).
[28] J. Sepioł, B, Kawałek and J. Mirek, *Ibid.* 701 (1977).
[29] J. Sepioł, *Ibid.* 504 (1983).
[30] J. Sepioł, *Ibid.* 559 (1983).
[31] J. Sepioł, *Pol. J. Chem.* **53**, 695 (1979).
[32] H. Kauffmann, *Ber. Dtsch. Chem. Ges.* **50**, 515 (1917).
[33] J. Derkosch and F. Langer, *Mh. Chem.* **86**, 924 (1955).
[34] K. Dimroth and G. Neubauer, *Chem. Ber.* **92**, 2042 (1959).
[35] G. Jones, *Org. React.* **15**, 270 (1967).
[36] E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum and D. R. Maulding, *J. Org. Chem.* **27**, 4428 (1962).
[37] L. Horner and K. Klüpfel, *Liebigs Ann. Chem.* **591**, 69 (1955).
[38] G. P. Schiemenz, *Chem. Ber.* **95**, 483 (1962).
[39] D. T. Mowry, *J. Am. Chem. Soc.* **67**, 1050 (1945).
[40] E. Campaigne, D. R. Maulding and W. L. Roelofs, *J. Org. Chem.* **29**, 1543 (1964).
[41] H. D. Edwards, F. P. Doyle and S. J. Palling, U.S. Pat. 2,839,402; *Chem. Abstr.* **53**, 943 (1959).