SYNTHESIS OF 3,5-DICYANO-4-PHENYL-2,6-BIS(4-*p*-TERPHENYLYL)--1,4-DIHYDROPYRIDINE. AN ATTEMPT AT EXTENDING THE HANTZSCH SYNTHESIS*

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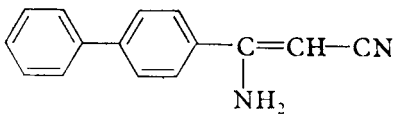
Received October 25th, 1984

The 3-oxopropanenitrile *IIIc*, prepared from 4-acetyl-*p*-terphenyl (*IV*) by the sequence *IV* → → *V* → *VI* → *IIIc*, reacts with benzaldehyde and ammonium acetate in acetic acid to give the Hantzsch 1,4-dihydropyridine *VIIc* and the corresponding pyridine derivative *VIIIc*. The alternative cyclocondensation of benzylidene derivative *IIc* and 3-oxopropanenitrile *IIIc* in the presence of ammonium acetate exclusively gives the pyridine derivative *VIIIc*. Rate of thermal and oxidative aromatizations of the 1,4-dihydropyridine derivatives, *VIIa*—*VIIc* → *VIIIa*—*VIIIc*, decreases in the order *VIIc* > *VIIb* > *VIIa*. Mechanism of these transformations and spectral characteristics of compounds *VIIc* and *VIIIc* are discussed with regard to their molecular structure.

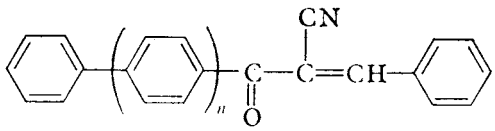
Our previous communications[1,2] showed that modified Hantzsch syntheses starting from the precursors type *I* and *IIb* represent efficient methods of preparation of symmetrically and unsymmetrically substituted 1,4-dihydropyridine derivatives containing 4-biphenylyl group(s) at 2 and/or 6 positions. Other possible approaches to substances of this type started from oxonitrile *IIIb*. Cyclocondensation of *IIIb* with benzaldehyde and ammonium acetate or condensation of oxonitriles *IIb* and *IIIb* by the method described by Zecher and Kröhnke[3] gave 2,6-bis(4-biphenylyl)-1,4--dihydropyridine (*VIIb*). The aim of this communication was to apply the experience from the synthesis of 1,4-dihydro derivative *VIIb* to preparation of analogous 1,4-dihydropyridine with *p*-terphenylyl group at 2 and 6 positions. In the context of investigation of physical and chemical properties of this type of 2,6-diaryl derivatives, we were interested in the problem of fluorescence, *i.e.* whether or not solutions of these compounds with extended conjugated system would exhibit fluorescence which was not observed with the 1,4-dihydropyridines type *VIIb* at room temperature[1]. At the same time, synthesis of the 1,4-dihydro derivative *VIIc* (containing 52 non-hydrogen atomic centres) would represent the so far greatest dimension of the Hantzsch synthesis[4,5].

* Part LX in the series On Dihydropyridines; Part LIX: This Journal *49*, 2620 (1984).

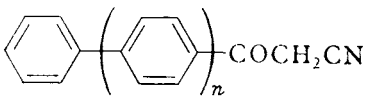
As the attempts at preparation of the *p*-terphenyl analogue of enaminonitrile *I* from 4-cyano-*p*-terphenyl[6] and acetonitrile or oxonitrile *IIIc* and ammonium acetate by the procedures used successfully[1,7] in preparation of 3-amino-3-(4-biphenylyl)--2-propenenitrile (*I*) failed for reasons not well understood by us, the oxonitriles *IIc* and *IIIc* were used as potential precursors of synthesis of compound *VIIc*. We decided to try the synthesis of the required oxonitrile *IIIc* by application of the general principle of synthesis of 3-oxopropanenitriles from isoxazoles[8,9]. Isoxazole *VI* was



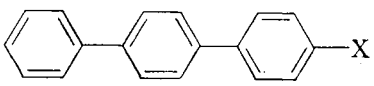
I



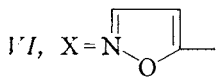
IIa, $n = 0$
IIb, $n = 1$
IIc, $n = 2$



IIIa, $n = 0$
IIIb, $n = 1$
IIIc, $n = 2$



IV, X = $COCH_3$
V, X = $COCH{=}CHN(CH_3)_2$
VI, X =



synthetized by application of the method[10] starting from acetylaromatic derivatives to 4-acetyl-*p*-terphenyl (*IV*). This compound was transformed with dimethylformamide dimethylacetal into the enamine *V* which, on reaction with hydroxylamine hydrochloride, gave the isoxazole derivative *VI* in good yield. The isoxazole ring opening of compound *VI* with sodium methoxide[8,9] gave the sodium salt which reacted with acetic acid to give the nitrile *IIIc* in a very good yield. The Knoevenagel condensation of the oxonitrile *IIIc* with benzaldehyde catalyzed with piperidine[11] produced the nitrile *IIc*. Surprisingly, the version of the Hantzsch synthesis consisting in cyclocondensation of two mol of compound *IIIc* with benzaldehyde in the presence of ammonium acetate gave, besides the expected 1,4-dihydro derivative *VIIc* (38%), also the corresponding pyridine *VIIIc* (17%). Another version of the same synthesis using the components *IIc*, *IIIc*, and ammonium acetate in a methanol-dimethylformamide mixture even gave exclusively the 3,5-dicyano-4-phenyl-2,6-bis-(4-*p*-terphenylyl) pyridine *VIIIc* (24%), and the presence of 1,4-dihydro derivative *VIIc* was not proved at all (TLC). As the attempts at preparing *p*-terphenyl analogue

of compound *I* failed, it is presumed that the first step of the two cyclocondenzations realized consists in the Michael addition of oxonitrile *IIIc* to the activated double bond of 2-benzylidene-3-oxopropanenitrile *IIc*, the heterocyclic ring closure taking place later. In accordance therewith the compound *IIc* was identified by TLC (Silufol, chloroform) of the reaction mixture obtained by short boiling of oxonitrile *IIIc*, benzaldehyde, and ammonium acetate in acetic acid. It is known that aldol condensation of an aldehyde with a component containing active methylene group represents the initial step of the whole classical Hantzsch synthesis[4,5,12].

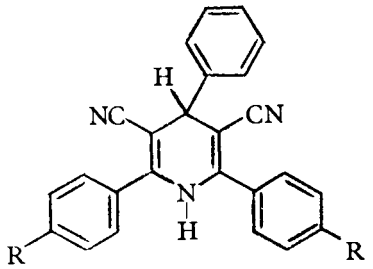
The surprising fact that the both above-mentioned versions of the Hantzsch synthesis also produce pyridine *VIIIc* can be explained by thermal and oxidative lability of the 1,4-dihydropyridine *VIIc*. On heating above its melting point (181–186°C) the 1,4-dihydropyridine *VIIc* is thermally quantitatively decomposed into the pyridine *VIIIc* (m.p. 318–320°C). In this context, the problem was interesting whether the thermal dehydrogenation is a specific feature of compound *VIIc* or a general characteristic of the series of 2,4,6-triaryl-3,5-dicyano-1,4-dihydropyridines *VII*. In order to solve this problem, all compounds of the series were submitted to thermolysis at 285–295°C under the same conditions. The results obtained (Table I) indicate that the thermal dehydrogenation really represents a general characteristic of 1,4-dihydropyridine derivatives of this type, its rate obviously depending on magnitude of the aryl groups at 2 and 6 positions of the 1,4-dihydropyridine skeleton and decreasing in the order *VIIc* > *VIIb* > *VIIa*. Possible disproportionation of the starting compounds *VII*, which would also produce the pyridines *VIII*, was excluded by spectral analysis (^{1}H NMR, IR) of the reaction mixture. The thermolysis carried out under argon gives lower yields of the pyridines in all the cases, which could indicate participation of air oxygen. But even the spontaneous dehydrogenation course (which could be explained by a cyclic mechanism of the boat conformation *IX* with equatorial 4-phenyl group, this conformation being forced just by the bulky 2,6-substituents in 2,6-diaryl-1,4-dihydropyridines *VII* – see Scheme 1) cannot be

TABLE I

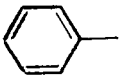
Composition of the mixture after thermolysis of 2,6-diaryl-3,5-dicyano-4-phenyl-1,4-dihydropyridines *VIIa*–*VIIc* (in %)

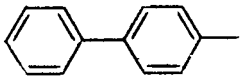
Starting compound	Atmosphere			
	air		argon	
VIIa	74 (*VIIa*)	26 (*VIIIa*)	79 (*VIIa*)	21 (*VIIIa*)
VIIb	5 (*VIIb*)	95 (*VIIIb*)	54 (*VIIb*)	46 (*VIIIb*)
VIIc	0 (*VIIc*)	100 (*VIIIc*)	3 (*VIIc*)	97 (*VIIIc*)

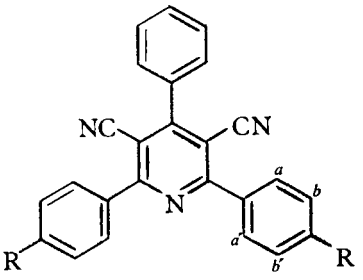
unambiguously excluded. The existence of the boat form can be inferred from the analogy with 3,5-diethoxycarbonyl-2,6-diphenyl-1,4-dihydropyridine whose boat conformation (in solid state) was proved by X-ray diffraction[13]. The thermal dehydrogenation of 1,4- dihydropyridines *VII* observed by us represents a case of aromatization



VII a, R = H

VII b, R = 

VII c, R = 

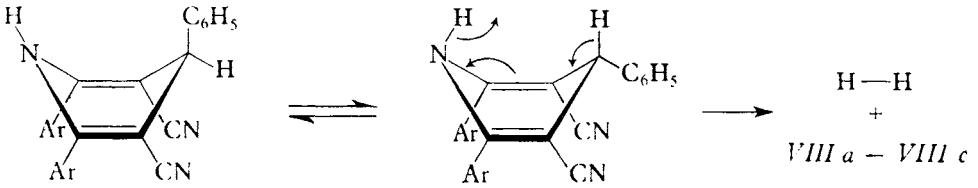


VIII a – VIII c

of N-non-substituted 1,4-dihydropyridines not known yet. Known cases of thermal aromatization involve N-substituted derivatives which give the respective pyridine derivative and hydrocarbon by splitting off of the 1-substituent[14–16]. In some older papers[17–19] describing cases of aromatization of N-non-substituted 1,4-dihydropyridines it is not quite clear whether the reaction is a surface oxidation or disproportionation. Increasing linear chains of benzene nuclei at 2 and 6 positions increase melting points of pyridines *VIII*, whereas the opposite is true of the corresponding 1,4-dihydropyridines *VII*, the lowest melting point being observed with 2,6-bis(4-*p*-terphenylyl)-1,4-dihydropyridine (*VIIc*). The same trend is observed in solubility of compounds *VII* in chloroform and benzene: *VIIc* > *VIIb* > *VIIa*.

Spectral characteristics of 1,4-dihydropyridine *VIIc* and pyridine *VIIIc* agree with the structure proposed. IR spectrum of *VIIc* only shows a single absorption band at 3 430 cm^{-1} of ν(N—H) vibration, and ^{1}H NMR spectrum contains a sharp signal of N—H proton at 6·51δ, which indicates the absence of intermolecular hydrogen bond due obviously to sterical reasons. A similar effect was observed[1] with 4-aryl-1,4-dihydropyridines type *VIIb*. It is an interesting phenomenon that even the 1,4-dihydropyridine *VIIc* – the highest representative of this type – does not exhibit solution fluorescence at room temperature. It only exhibits fluorescence in solid state after irradiation with UV light (which is similar to the lower derivatives *VIIa* and *VIIb*). On the contrary, the corresponding pyridine derivative *VIIIc* shows

distinct fluorescence both in solution and in solid state. The same is true of *VIIIb*, whereas fluorescence of *VIIIa* is very weak. The solution fluorescence of compound *VIIIc* exhibits distinct solvatochromism. Increasing polarity of solvent causes bathochromic shift of the fluorescence: violet (benzene), blue (chloroform, carbon disulphide), green (acetonitrile, dimethylformamide).



VII a – VII c *IX a – IX c*

SCHEME 1

These different optical properties of compounds *VII* and *VIII* do not contradict the hypothesis[20,21] that the most intensive fluorescence is exhibited by the compounds whose S_1 state is as much conjugated as possible. Comparison of ^{1}H NMR spectra of pyridine *VIIIc* and the respective 1,4-dihydroderivative *VIIc* in the region of aromatic proton signals reveals besides a complex multiplet also a characterized localized signal at 8·20δ which is observed with pyridines *VIIIa* (8·04δ) and *VIIIb* (8·18δ), too. These signals with integral intensity corresponding to four protons were asasigned to the *ortho* protons $H_{a,a'}$, (see formulae *VIII*) on the basis of analogy with the ^{1}H NMR spectra of 4-aryl-2-(4-biphenylyl)-3-cyanocycloalkeno[*b*]pyridines[7] and 2,4,6-triaryl-3-cyanopyridines[22]. Their simple shape is probably due to the non-planar solution conformation of molecules *VIII* in S_0 state, in which these protons become chemically equivalent due to distinct deviation (rotation) of 2 and 6 phenyl groups. The absence of these signals from spectra of the 1,4-dihydropyridines *VII* indicates a greater conformational coplanarity and, hence, conjugation of aryl groups with the 1,4-dihydropyridine skeleton in the S_0 states. In the S_1 excited state the pyridine molecules probably become more coplanar due to increased resonance interaction between pyridinoid and benzenoid rings imparting a certain double bond character to the bonds connecting the aromatic nuclei, which – according to the hypothesis[20,21] – results in the fluorescence observed. Obviously this situation is analogous to that of polyphenyls[23–25] structurally close to the compounds *VIII* studied. So *e.g.* *p*-terphenyl, which has non-planar conformation in solution[26,27], is – most likely – approximately coplanar in its excited state, and it exhibits distinct fluorescence[24,28]. On the contrary, with the 1,4-dihydropyridines *VII* the conjugation degree in the S_1 state is probably lower than that in S_0 due to complex conformation of the heterocyclic ring, which could explain the suppression of the solution fluores-

cence by non-radiative energy exchange with the solvent molecules. Therefore, they only exhibit weak fluorescence in crystalline state (where the conformational mobility of the molecules is suppressed).

EXPERIMENTAL

The temperature data are not corrected. The melting points were determined with a Boetius apparatus. The spectral characteristics were measured with the following apparatus: Perkin Elmer 325 (IR), Carl Zeiss Jena Specord UV VIS (UV), and Varian XL-100 (^{1}H NMR, tetramethylsilane as internal standard). 2,6-Diaryl-4-phenyl-3,5-dicyanopyridines *VIIIa*, *VIIIb* were prepared by oxidation of the respective 1,4-dihydro derivatives *VIIa*, *VIIb* (2 mmol) with nitrous acid[29].

2,4,6-Triphenyl-3,5-dicyanopyridine (*VIIIa*)

Yield 85%, m.p. 244–246°C (ref.[3] gives m.p. 238°C). IR spectrum (chloroform), $\tilde{\nu}_{max}$ (cm^{-1}): 3 070 w, 3 020 m (=C—H), 2 235 m (C≡N), 1 602 w, 1 581 w, 1 539 s, 1 526 s, 1 491 m, 1 447 m (C=C$_{arom}$ and pyridine skeleton). ^{1}H NMR spectrum (C^{2}HCl$_3$), δ (ppm): 8·04 (m, 4 H, 2 × H$_{a,a'}$), 7·40–7·68 (m, 11 H, H$_{arom}$).

2,6-Bis(4-biphenylyl)-4-phenyl-3,5-dicyanopyridine (*VIIIb*)

Yield 98%, m.p. 271–273°C. For $C_{37}H_{23}N_3$ (509·6) calculated: 87·19% C, 4·56% H, 8·25% N; found: 86·89% C, 4·57% H, 8·24% N. IR spectrum (chloroform), $\tilde{\nu}_{max}$ (cm^{-1}): 3 070 w, 3 010 m (=C—H), 2 230 (C≡N), 1 613 m, 1 605 m, 1 585 w, 1 566 m, 1 540 s, 1 484 m, 1 445 m (C=C$_{arom}$ and pyridine skeleton). ^{1}H NMR spectrum (C^{2}HCl$_3$), δ (ppm): 7·38–7·71 (m, 15 H, H$_{arom}$), 7·77 (d, 4 H, 2 × H$_{b,b'}$, J = 8·2 Hz), 8·18 (d, 4 H, 2× H$_{a,a'}$, J = 8·2 Hz).

2,4,6-Triphenyl-3,5-dicyano-1,4-dihydropyridine (*VIIa*)

A mixture of 2·33 g nitrile *IIa*, 1·45 g nitrile *IIIa*, and 0·75 g ammonium acetate in 20 ml methanol was boiled 8 h and left to stand overnight. The separated solid was collected by suction, washed with ethanol, and recrystallized from a dioxane–ethanol mixture. Yield 2·4 g (67%), m.p. 279 to 281°C (ref.[3] gives m.p. 268°C, ref.[30] gives m.p. 279–280°C). IR spectrum (KBr disc), $\tilde{\nu}_{max}$ (cm^{-1}): 3 264 m, 3 222 m (N—H), 3 102 m, 3 037 w, 3 010 w, 2 992 w (=C—H), 2 210 s, 2 200 s (C≡N), 1 643 s, 1 601 m, 1 578 m, 1 540 w, 1 500 s, 1 456 m, 1 449 m (C=C$_{arom}$ and 1,4-dihydropyridine skeleton). ^{1}H NMR spectrum (hexadeuteriodimethyl sulphoxide), δ (ppm): 4·65 (s, 1 H, H—C$_{(4)}$), 7·20–7·78 (m, 15 H, H$_{arom}$), 9·97 (s, 1 H, N—H).

2,6-Bis(4-biphenylyl)-3,5-dicyano-4-phenyl-1,4-dihydropyridine (*VIIb*)

A) A mixture of 1·1 g oxonitrile *IIIb*, 0·32 g benzaldehyde, and 1·5 g ammonium acetate in 2 ml acetic acid was boiled 5 h. The separated solid was collected by suction, washed with ethanol, and recrystallized from an ethanol–benzene mixture. Yield 0·9 g *VIIb* (71%), m.p. 268–270°C (ref.[1] gives m.p. 270–272°C).

B) A mixture of 0·42 g nitrile *IIb*, 0·3 g nitrile *IIIb*, and 0·1 g ammonium acetate in 5 ml acetic acid was boiled 5 h. The product was treated as sub *A*) to give 0·55 g *VIIb* (79%), m.p.

268–270°C. Identity of the 1,4-dihydropyridines prepared by the two procedures was confirmed by comparison of their spectral characteristics with those of a sample prepared by cyclocondensation of enaminonitrile *I* with benzaldehyde[1].

3-Dimethylamino-1-(4-*p*-terphenylyl)-2-propen-1-one (*V*)

A suspension of 12 g 4-acetyl-*p*-terphenyl[31] (*IV*) and 14 g dimethylformamide dimethylacetal in 20 ml dimethylformamide was heated at 150–160°C 6 h. The yellow precipitate obtained by cooling was collected by suction, washed with ethanol, and recrystallized from dioxane. Yield 11·4 g (79%), m.p. 235–241°C. For $C_{23}H_{21}NO$ (327·5) calculated: 84·36% C, 6·48% H, 4·28% N; found: 84·14% C, 6·62% H, 4·30% N. IR spectrum (chloroform), $\tilde{\nu}_{max}$ (cm^{-1}): 3 016 m (=C—H), 1 644 s (C=O), 1 610 m, 1 578 s, 1 560 m, 1 542 m, 1 477 m $(C=C)_{arom}$, 1 360 s (CH_3). ^1H NMR spectrum (C^2HCl_3), δ (ppm): 3·03 (br.s, 6 H, 2× CH_3), 5·73 (d, 1 H, =CH—N, $^3J_{HH}$ = 12 Hz), 7·25–8·17 (m, 14 H, H_{arom} and =CH—CO).

5-(4-*p*-Terphenylyl)isoxazole (*VI*)

A suspension of 1·4 g enamine *V* and 0·45 g hydroxylamine hydrochloride in a mixture of 20 ml dioxane and 6 ml water was stirred at room temperature 8 h. Then it was left to stand overnight and diluted with 100 ml water. The separated solid was collected by suction, washed with water and ether, and recrystallized from an ethanol–dimethylformamide mixture. Yield 0·9 g (71%), m.p. 245–248°C (decomposition). For $C_{21}H_{15}NO$ (297·4) calculated: 84·81% C, 5·09% H, 4·71% N; found: 84·84% C, 5·19% H, 4·49% N. IR spectrum (chloroform), $\tilde{\nu}_{max}$ (cm^{-1}): 3 010 m (=C—H), 1 613 m, 1 484 m, 1 459 s (isoxazole skeleton and $C=C_{arom}$). ^1H NMR spectrum (C^2HCl_3), δ (ppm): 6·45 (s, 1 H, H—$C_{(3)}$), 7·21–7·87 m (m, 13 H, H_{arom}), 8·19 (d, 1 H, H—$C_{(4)}$), $^3J_{HH}$ = 3·6 Hz.

3-(4-*p*-Terphenylyl)-3-oxopropanenitrile (*IIIc*)

A solution of 70 mg sodium in 35 ml methanol was treated with 0·9 g isoxazole derivative *VI*, and the suspension was boiled 2 h. After cooling, the mixture was acidified with 10 ml acetic acid. The separated solid was collected by suction, washed with water and ether, and recrystallized from dimethyl sulphoxide. Yield 0·8 g (89%), m.p. 224–229°C (decomposition). For $C_{21}H_{15}NO$ (297·4) calculated: 84·81% C, 5·39% H, 4·71% N; found: 84·31% C, 5·07% H, 4·86% N. IR spectrum (KBr disc), $\tilde{\nu}_{max}$ (cm^{-1}): 2 255 w (C≡N), 1 695 s(C=O), 1 601 s, 1 485 m $(C=C)_{arom}$. ^1H NMR spectrum (hexadeuteriodimethyl sulphoxide,100°C), δ (ppm): 4·60 (s, 2H, CH_2), 7·20–8·20 (m, 13 H, H_{arom}).

2-Benzylidene-3-(4-*p*-terphenylyl)-3-oxopropanenitrile (*IIc*)

Two drops of piperidine was added to a mixture of 0·6 g oxonitrile *IIIc*, 0·21 g benzaldehyde *I*, and 20 ml methanol, and the mixture was boiled 1 h, stirred at room temperature 6 h, and the separated solid was collected by suction, washed with methanol, and recrystallized from an ethanol–dioxane mixture. Yield 0·52 g (67%), m.p. 238–242°C, R_F 0·41 (Silufol, chloroform). For $C_{28}H_{19}NO$ (385·5) calculated: 87·24% C, 4·98% H, 3·63% N; found: 87·12% C, 5.01% H, 3·57% N. IR spectrum (chloroform), $\tilde{\nu}_{max}$ (cm^{-1}): 3 060 w, 3 010 m (=C—H), 2 209 w (C≡N), 1 667 m (C=O), 1 603 s, 1 568 m, 1 484 m, 1 449 m $(C=C)_{arom}$. ^1H NMR spectrum (C^2HCl_3), δ(ppm): 7·31–8·17 (m, 19 H, H_{arom} and =CH).

3,5-Dicyano-4-phenyl-2,6-bis(4-*p*-terphenylyl)-1,4-dihydropyridine (*VIIc*)

A mixture of 0·59 g oxonitrile *IIIc*, 0·11 g benzaldehyde, and 0·6 g ammonium acetate in 5 ml acetic acid was boiled 24 h. The separated solid was collected by suction and washed with ethanol. The crystalline product (0·5 g) was submitted to column chromatography (80 g silica gel, chloroform). The individual fractions were examined by TLC (Silufol, Kavalier; chloroform as eluent; detection in UV light and with iodine vapours). The first fraction was a light yellow solid exhibiting distinct blue fluorescence in chloroform solution; it was identified as pyridine *VIIIc* (R_F 0·59). Yield 110 mg (17%), m.p. 318–320° (benzene–chloroform). For $C_{49}H_{31}N_3$ (661·8) calculated: 88·92% C, 4·73% H, 6·35% N; found: 88·63% C, 5·21% H, 6·26% N. UV spectrum (acetonitrile), λ_{max} (log ε): 204 nm (5·16), 265 (4·71), 332 (4·84). IR spectrum (chloroform), $\tilde{\nu}_{max}$ (cm^{-1}): 3 065 w, 3 034 m, 3 012 m (=C—H), 2 227 m (C≡N), 1 608 m, 1 590 m, 1 570 w, 1 552 w, 1 534 s, 1 486 s (pyridine skeleton and C=C_{arom}). ^{1}H NMR spectrum (C^2HCl_3), δ (ppm): 7·29–7·97 (m, 27 H, H_{arom}), 8.20 (d, 4 H, 2× $H_{a,a'}$, J = 8·2 Hz). Further elution with chloroform gave 250 mg (38%) 1,4-dihydropyridine *VIIc* (R_F 0·30), m.p. 181–186°C (ethanol–benzene). For $C_{49}H_{33}N_3$ (663·9) calculated: 88·65% C, 5·02% H, 6·33% N; found: 83·30% C, 5·29% H, 6·18% N. UV spectrum (ethanol), λ_{max} (nm) (log ε): 205 (5·18), 301 (4·90), 357 inflection (3·82). IR spectrum (chloroform), $\tilde{\nu}_{max}$ (cm^{-1}): 3 430 m (N—H), 3 072 w, 3012 m (=C—H), 2 202 s (C≡N), 1 645 m, 1 604 m, 1 472 s (1,4-dihydropyridine skeleton and C=C_{arom}). ^{1}H NMR spectrum (C^2HCl_3), δ (ppm): 4·60 (s, 1 H, H—$C_{(4)}$), 6·51 (s, 1 H, N—H), 7·28–8·00 (m, 31 H, H_{arom}).

3,5-Dicyano-4-phenyl-2,6-bis(3-*p*-terphenylyl)pyridine (*VIIIc*)

A mixture of 0·64 g 2-benzylidene-3-oxopropanenitrile *IIc*, 0·5 g oxonitrile *IIIc*, and 0·55 g ammonium acetate in 5 ml methanol and 10 ml dimethylformamide was boiled 24 h. The solid separated on cooling was collected by suction, washed with ethanol, and recrystallized from benzene. Yield 0·26 g (24%) pyridine *VIIIc*, m.p. 306–310°C, after purification by column chromatography (silica gel, chloroform) m.p. 318–320°C. The identity of compound *VIIIc* was confirmed by comparison of its spectral characteristics with those of the sample prepared in the previous case.

Thermal Dehydrogenation of 1,4-Dihydropyridines *VIIa–VIIc*

20 mg compound *VIIc* (or 150 mg *VIIb* or *VIIa*) was heated at 285–295°C 3 h. ^{1}H NMR spectra of the products were measured, and quantitative proportions of unreacted *VII* and pyridine *VIII* were determined. The thermal treatment under argon was carried out in the same way. The results are summarized in Table I.

The authors are indebted to workers of Department of Organic Analysis (Dr L. Helešic, Head) for the analyses carried out, and to workers of Central Laboratories of the Institute for the measurements of spectral characteristics.

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Translated by J. Panchartek.