

SYNTHESIS OF CYANO DERIVATIVES WITH DIAZAQUATERPHENYL SKELETON

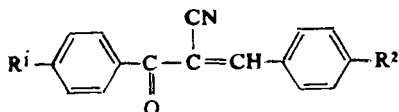
Štefan MARCHALÍN and Josef KUTHAN

*Department of Organic Chemistry,
Prague Institute of Chemical Technology, 166 28 Prague 6*

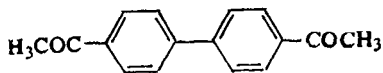
Received August 13th, 1984

Cyclocondensation of 3-aryl-2-arylmethylene-3-oxopropanenitriles *I* with 4,4'-diacetyl biphenyl (*II*) in the presence of ammonium acetate gives *para*-substituted 4'-acetyl-3,5-diphenyl-2-aza-1:1',4':1''-terphenyls *III* and 4,4''-dicyano-3,3''',5,5'''-tetraphenyl-2,2'''-diaz-1:1',4':1''',4''':1''''-quaterphenyls *IV*. Analogous reaction of the acetyl derivative *IIIe* with the oxonitriles *Ie* and *Ia* afforded the corresponding products *IVe* and *I'*.

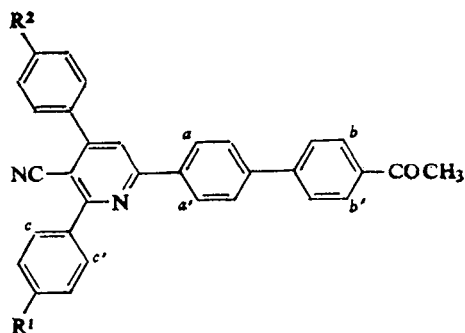
Recently, 3-aryl-2-arylmethylene-3-oxopropanenitriles of the type *I* have been employed in the synthesis of condensed 4*H*-pyrans¹⁻³, 4-aryl-3-cyano-2-pyridones^{4,5}, 4,6-diaryl-3,5-dicyano-2-thioxopyridines^{6,7} and unsymmetrically substituted 1,4-dihydropyridines^{8,9}. In our preceding communications we reported the preparation of cycloalkeno[*b*]pyridines¹⁰ and 2,4,6-triaryl-3-cyanopyridines¹¹ by cyclocondensations of the oxonitrile *I* with carbonyl methylene components in the presence of ammonium acetate. In this context, it was of interest whether this synthetic scheme might be applied to 4,4'-diacetyl biphenyl (*II*) which should give conjugated pyridine derivatives of the polyphenylene type.



- Ia*, R¹ = H, R² = H *Id*, R¹ = CH₃, R² = CH₃
Ib, R¹ = H, R² = CH₃ *Ie*, R¹ = C₆H₅, R² = H
Ic, R¹ = CH₃, R² = H *If*, R¹ = C₆H₅, R² = CH₃



II

*IIIa – IIIf*

We found that cyclocondensation reaction of 3-aryl-2-arylmethylene-3-oxo-propanenitriles *Ia–If* with 4,4'-diacetylbiphenyl (*II*) in the presence of ammonium acetate afforded a mixture of *para*-substituted 4''-acetyl-3,5-diphenyl-2-aza-1 : 1',4' : 1''-terphenyls *IIIa–III f* and 4,4''-dicyano-3,3''',5,5'''-tetraphenyl-2,2'''-diaz-1 : 1',4' : 1''-quaterphenyls *IVa–IVf*. Crystallization from dimethylforma-

TABLE I
para-Substituted 4''-acetyl-3,5-diphenyl-2-aza-1:1',4':1''-terphenyls *IIIa–III f*

Compound (yield, %) ^b	R ¹	R ²	M.p., °C ^a	Formula (mol.wt.)	Calculated/Found		
					% C	% H	% N
<i>IIIa</i> (41)	H	H	253–255	C ₃₂ H ₂₂ N ₂ O (450.6)	85.30	4.93	6.22
					85.22	4.96	6.27
<i>IIIb</i> (36)	H	CH ₃	299–301	C ₃₃ H ₂₄ N ₂ O (464.6)	85.31	5.22	6.03
					85.03	5.37	5.97
<i>IIIc</i> (19)	CH ₃	H	250–252	C ₃₃ H ₂₄ N ₂ O (464.6)	85.31	5.22	6.03
					85.01	5.30	6.10
<i>III d</i> (19)	CH ₃	CH ₃	280–282	C ₃₄ H ₂₆ N ₂ O (478.6)	85.32	5.49	5.85
					84.55	5.64	5.60
<i>IIIe</i> (57)	C ₆ H ₅	H	222–224	C ₃₈ H ₂₆ N ₂ O (526.7)	86.66	4.99	5.32
					86.50	5.09	6.26
<i>III f</i> (46)	C ₆ H ₅	CH ₃	207–210	C ₃₉ H ₂₈ N ₂ O (540.7)	86.63	5.23	5.18
					86.68	5.29	5.09

^a Compounds *IIIa*, *IIIc*, *IIIe*, and *III f* were crystallized from ethanol–benzene, *IIIb* and *III d* from benzene; ^b based on diacetyl derivative *II*.

amide or column chromatography on silica gel in chloroform gave the compounds *III* and *IV* in the yields 19–57% and 13–28%, respectively (see Tables I and II). The reaction conditions were first investigated for the reaction of 2-benzylidene-3-(4-biphenyl)-3-oxopropanenitrile (*Ie*) with the diacetyl derivative *II*. The reaction course is substantially influenced by the solvent. In aprotic solvents such as acetonitrile, benzene or tetrahydrofuran, no pyridine derivatives *IIIa* and *IVe* are formed and the

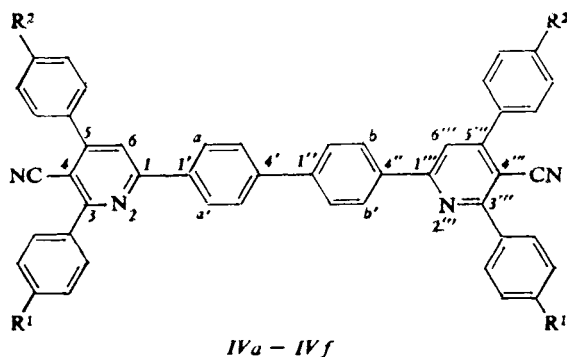


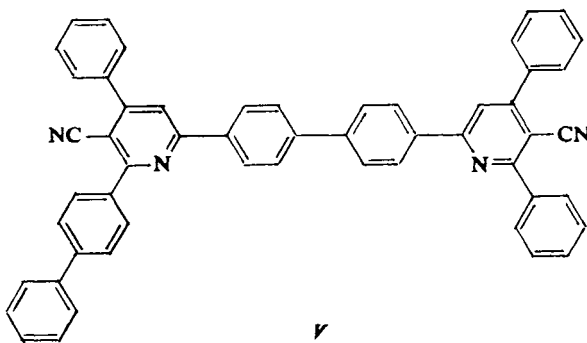
TABLE II

para-Substituted 4,4''-dicyano-3,3''',5,5'''-tetraphenyl-2,2'''-diazia-1:1',4':1'',4''':1''''-quaterphenyls *IV*

Compound (Yield, %) ^b	R ¹	R ²	M.p., °C ^a	Formula (Mol.wt.)	Calculated/Found		
					% C	% H	% N
<i>IVa</i> (13)	H	H	342–344	C ₄₈ H ₃₀ N ₄ (662·8)	86·97	4·57	8·45
					86·79	4·64	8·52
<i>IVb</i> (17)	H	CH ₃	345–346	C ₅₀ H ₃₄ N ₄ (690·9)	86·92	4·97	8·11
					86·80	5·26	7·96
<i>IVc</i> (18)	CH ₃	H	325–327	C ₅₀ H ₃₄ N ₄ (690·9)	86·92	4·97	8·11
					86·71	5·36	8·17
<i>IVd</i> (28)	CH ₃	CH ₃	>370	C ₅₂ H ₃₈ N ₄ (718·9)	86·87	5·34	7·79
					86·55	5·43	7·62
<i>IVe</i> (24)	C ₆ H ₅	H	335–337	C ₆₀ H ₃₈ N ₄ (815·0)	88·42	4·71	6·87
					87·89	4·66	6·63
<i>IVf</i> (12)	C ₆ H ₅	CH ₃	344–346	C ₆₂ H ₄₂ N ₄ (843·1)	88·32	5·03	6·65
					88·15	5·17	6·49

^a Compounds *IVa*, *IVe*, and *IVf* were crystallized from dimethylformamide, *IVb–IVd* from benzene; ^b based on the diacetyl derivative *II*.

unreacted *II* was quantitatively recovered from the reaction mixture. A mixture of ethanol and dimethylformamide proved to be the medium of choice: the products *IIIe* and *IVe* separate from the reaction mixture, their ratio depending on the ratio of the starting compounds. Reaction of two mols of *Ie* with one mol of *II* gave 57% of *IIIe* and 24% of *IVe*, whereas equimolar amounts of the reactants afforded 32% of *IIIe* and 4% of *IVe*. The assumption that the acetyl derivatives *III* are intermediates in the preparation of *para*-substituted 4,4''-dicyano-3,3''',5,5'''-tetraphenyl-2,2''-diaz-1 : 1',4' : 1'',4'' : 1'''-quaterphenyls *IV* was confirmed by cyclocondensation of compound *IIIe* with the precursors *Ia* and *Ie* in the presence of ammonium acetate. Both reactions gave the corresponding polyphenylene pyridines, *i.e.* compound *IVe* and the unsymmetrically substituted derivative *V*. For the reasons discussed in our preceding work¹¹ the attempted isolation of the possible primarily formed dihydro derivatives failed.



In the common solvents, compounds *IVa-IVf* and *V* exhibit a marked blue fluorescence which occurs also upon UV-irradiation of the solid substances. Both IR and ¹H NMR spectra agree with the structures *III-V*. The acetyl derivatives (Table III) have IR-bands due to C≡N stretching vibrations at 2 220–2 222 cm⁻¹, C=O vibrations at 1 672–1 682 cm⁻¹ and bands characteristic of ν(C=C)_{arom} and a pyridine skeleton. The ¹H NMR spectra display a singlet of an acetyl group at δ 2.56–2.63. The *para*-substituted 4,4''-dicyano-3,3''',5,5'''-tetraphenyl-2,2''-diaz-1 : 4',4' : 1'',4'' : 1'''-quaterphenyls *IV* (Table IV) and *V* showed C≡N bands at 2 119–2 221 cm⁻¹ and bands due to benzene and pyridine rings at 1 446–1 612 cm⁻¹ in the IR spectra. Their ¹H NMR spectra (Table IV) exhibited complex multiplets at δ 7.17–8.30. Compounds *III* and *IV* showed signals at δ 8.22–8.47 and δ 7.86–8.23 which were ascribed to the *ortho*-protons H_a, H_b, and H_c on the basis of comparison with the spectra of 4-aryl-2-(4-biphenyl)-3-cyanocycloalkeno[*b*]pyridines¹⁰, 2,4,6-triaryl-3-cyanopyridines¹¹ and 4,4'-diacetylbiphenyl (*II*). The character of these signals indicates that, in solution, the rings are not coplanar, similarly to the case of 2,4,6-triaryl-3-cyanopyridines¹¹.

TABLE III
Infrared and ^1H NMR data for acetyl derivatives *IIIa*–*IIIf*

Com- pound	$\tilde{\nu}_{\text{max}}, \text{cm}^{-1}$ (CHCl_3) ^a				$\delta_{\text{H}}, \text{ppm}$ ($\text{C}^2\text{HCl}_3, 31^\circ\text{C}$) ^b				
	$\nu(\text{C}=\text{H})$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$	$\text{H}_{\text{a,a}}^{\text{c}}$	$\text{H}_{\text{b,b}'} + \text{H}_{\text{c,c}'}$	H_{arom}	CH_3CO	CH_3
<i>IIIa</i>	3 016 w	2 220 m	1 680 s	1 605 s 1 556 w 1 492 m 1 585 s 1 531 s 1 446 w 1 574 s	8·25 d	7·90–8·12 m	7·28–7·88 m	2·63 s	—
<i>IIIb</i>	3 068 w 3 040 w	2 220 s	1 672 s	1 602 m 1 528 w 1 495 m 1 583 s 1 520 w 1 450 w 1 570 s 1 512 m	8·22 d	7·92–8·13 m	7·24–7·84 m	2·60 s	2·43 s
<i>IIIc</i>	3 016 m	2 222 m	1 681 s	1 606 s 1 532 s 1 495 m 1 584 s 1 514 m 1 447 w 1 570 s	8·24 d	7·86–8·11 m	7·25–7·84 m	2·62 s	2·43 s
<i>III d</i>	3 080 w 3 038 w	2 220 s	1 680 s	1 603 m 1 569 m 1 510 m 1 584 s 1 530 m	8·46 d	8·02–8·23 m	7·19–8·02 m	2·56 s	2·31 s
<i>IIIe</i>	3 010 w	2 221 m	1 681 s	1 605 s 1 556 w 1 489 m 1 578 s 1 530 s 1 450 w	8·26 d	7·94–8·20 m	7·30–7·88 m	2·63 s	—
<i>III f</i>	3 012 m	2 220 m	1 682 s	1 605 s 1 530 s 1 489 m 1 578 s 1 512 m 1 449 w 1 555 m	8·28 d	7·93–8·20 m	7·29–7·88 m	2·63 s	2·46 s

^a Compounds *IIIb* and *III d* measured by the KBr technique; ^b compound *III d* measured in pentadeuteriopyridine at 80°C ; ^c $J = 8\cdot2$ Hz.

TABLE IV
Infrared and ^1H NMR data for polyphenylene pyridines *IVa-IVf*

Compound	$\tilde{\nu}_{\text{max}}, \text{cm}^{-1}$ (KBr)			$\delta_{\text{H}}, \text{ppm}^a$		
	$\nu(\text{C}=\text{H})$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{N})$	$\text{H}_{\text{a,a}'}$ + $\text{H}_{\text{b,b}'}$ ^b	H_{arom}	CH_3
<i>IVa</i>	3 066 w 3 040 w	2 220 s	1 608 s 1 526 s 1 453 w 1 586 s 1 493 s 1 446 m 1 573 s	8·28 d	7·18—8·09 m	—
<i>IVb</i>	3 092 w 3 037 w	2 219 s	1 612 m 1 527 s 1 482 w 1 587 s 1 516 m 1 454 w 1 575 s 1 498 m	8·44 d	7·17—8·30 m	2·28 s
<i>IVc</i>	3 070 w 3 035 w	2 220 s	1 610 w 1 532 s 1 496 m 1 583 s 1 515 m 1 448 w 1 570 s	8·47 d	7·23—8·20 m	2·30 s
<i>IVd</i>	3 032 w	2 221 s	1 612 m 1 568 s 1 509 s 1 580 s 1 526 s	8·35 d	7·19—8·15 m	2·31 s
<i>IVe</i>	3 060 w 3 035 w	2 119 s	1 607 m 1 557 m 1 489 s 1 576 s 1 528 s 1 446 m	—	^c	—
<i>IVf</i>	3 032 w	2 220 s	1 610 s 1 528 s 1 490 s 1 576 s 1 510 s 1 450 m 1 556 m	—	^c	—

^a Compound *IVa* measured in hexadeuteriodimethyl sulfoxide at 140°C; other compounds in pentadeuteriopyridine at 80°C; ^b $J = 8\cdot2$ Hz; ^c not measured because of insufficient solubility.

EXPERIMENTAL

Temperature data are uncorrected. Melting points were determined on a Boetius block. Spectral data were obtained with Perkin-Elmer 325 (IR) and Varian XL-100 (^1H NMR; internal standard tetramethylsilane) instruments. The 3-aryl-2-arylmethylene-3-oxopropanenitriles *Ia*–*Id* were prepared by Knoevenagel condensation of 3-aryl-3-oxopropanenitriles¹² with the corresponding benzaldehydes according to ref.¹³. The following melting points were observed for the obtained compounds (reported values in parentheses): *Ia*: 84–85°C (83.5–85.5°C, ref.¹⁴), *Ib*: 89–90°C (89–90°C, ref.¹⁴), *Ic*: 97–98°C, (95–96°C, ref.¹⁵), and *Id*: 91–92°C. Preparation of the oxonitriles *Ie* and *If* is described in our earlier paper¹⁶. 4,4'-Diacetyl biphenyl (*II*) was obtained by acetylation of biphenyl according to ref.¹⁷, m.p. 190–192°C (reported¹⁷ m.p. 191°C). Infrared spectrum (chloroform), cm^{-1} : 1 685 s (C=O); ^1H NMR spectrum (C^2HCl_3), δ (ppm): 2.66 (s, 6 H, $2 \times \text{COCH}_3$), 7.72 (d, 4 H, H_{meta} , $J = 8.2$ Hz), 8.07 (d, 4 H, H_{ortho} , $J = 8.2$ Hz).

para-Substituted 4,4''-Dicyano-3,3''',5,5'''-tetraphenyl-2,2'''-diazia-1:1',4':1'',4'':1''''-quaterphenyls *IV*

A mixture of oxonitrile *I* (2 mmol), 4,4-diacetyl biphenyl (*II*; 1 mmol), ammonium acetate (2 mmol), ethanol (5 ml), and dimethylformamide (5 ml) was heated to 160°C for 14 h. After cooling, the precipitate was filtered, washed with water and ethanol and processed according to one of the following procedures.

A) The pyridines *IVa*, *IVe* and *IV*, were obtained by crystallization from dimethylformamide. The mother liquor was diluted with water, the precipitate filtered, washed with ethanol and the thus-obtained respective acetyl derivatives *IIIa*, *IIIe*, and *III* were crystallized from an appropriate solvent.

B) After crystallization from toluene, the mixture was separated by chromatography on a column of silica gel in chloroform (detection by iodine vapours and UV light). The polyphenylene pyridines (*IVb*–*IVd*) were obtained as a first fraction; further elution afforded the acetyl derivatives (*IIIb*–*III**d*). The yields of *III* and *IV*, solvents for crystallization, melting points, and analytical data are given in Tables I and II.

3,3''-Bis(4-biphenyl)-4,4''-dicyano-5,5'''-diphenyl-2,2'''-diazia-1:1',4':1'',4'':1''''-quaterphenyl (*IVe*)

A mixture of acetyl derivative *IIIe* (0.3 g), oxonitrile *Ie* (0.18 g), ammonium acetate (0.03 g), ethanol (5 ml) and dimethylformamide (5 ml) was heated to 160°C for 16 h. The precipitate was filtered, washed with ethanol and crystallized from dimethylformamide, yielding 0.19 g (41%) of *IVe*, m.p. 335–337°C. Its IR and ^1H NMR spectra were identical with those of the compound prepared by cyclocondensation of *Ie* with *II*.

3-(4-Biphenyl)-4,4''-dicyano-3,3''',5,5'''-triphenyl-2,2'''-diazia-1:1',4':1'',4'':1''''-quaterphenyl (*V*)

A mixture of acetyl derivative *IIIe* (0.5 g), oxonitrile *Ia* (0.22 g), ammonium acetate (0.07 g), ethanol (5 ml), and dimethylformamide (2 ml) was heated to 160°C for 12 h. The separated precipitate was filtered, washed successively with water and ethanol and crystallized from benzene, affording 0.34 g (48%) of *V*, m.p. 272–274°C. For $\text{C}_{54}\text{H}_{34}\text{N}_4$ (738.9) calculated: 87.77% C, 4.65% H, 7.58% N; found: 87.50% C, 4.60% H, 7.65% N. IR spectrum (KBr), cm^{-1} : 3 060 w, 3 035 w (C–H), 2 218 s (C≡N), 1 610 w, 1 583 s, 1 570 s, 1 556 m, 1 525 s, 1 486 m, 1 444 w (C=C and pyridine skeleton). ^1H NMR spectrum (C^2HCl_3), δ (ppm): 7.27–7.38 m (H_{arom}).

The authors are indebted to the staff of the Department of Elemental Analysis (Dr L. Helešic, Head) for performing the analyses. Their thanks are due also to the staff of the Central Laboratories of this Institute for spectral measurements.

REFERENCES

1. Abdou S., Fahmy S. M., Sadek K. U., Elnagdi M. H.: *Heterocycles* **16**, 2177 (1981).
2. Daboun H. A. F., Abdou S. E., Hussein M. M., Elnagdi M. H.: *Synthesis* **1982**, 502.
3. Elfahham H. A., Abdel-Galil F. M., Ibraheim Y. R., Elnagdi M. H.: *J. Heterocycl. Chem.* **20**, 667 (1983).
4. Seoane C., Soto J. L., Zamorano P., Quinteiro M.: *J. Heterocycl. Chem.* **18**, 309 (1981).
5. Khalifa M. A. E., Elbanany A. A., Tammam G. H.: *Curr. Sci.* **51**, 1112 (1982).
6. Rubio M. J., Seoane C., Soto J. L.: *Heterocycles* **20**, 783 (1983).
7. Encinas M. J. R., Seoane C., Soto J. L.: *Justus Liebigs Ann. Chem.* **1984**, 213.
8. Elgemeie G. E. H., Elees S. A., Elsakka I., Elnagdi M. H.: *Z. Naturforsch.* **38B**, 639 (1983).
9. Marchalín Š., Kuthan J.: *This Journal* **48**, 3123 (1983).
10. Marchalín Š., Kuthan J.: *This Journal* **49**, 1395 (1984).
11. Marchalín Š., Kuthan J.: *This Journal*, in press.
12. Eby C. J., Hauser C. R.: *J. Amer. Chem. Soc.* **79**, 723 (1957).
13. Kauffmann H.: *Ber. Deutsch. Chem. Ges.* **50**, 515 (1917).
14. Umeda T., Hirai E.: *Chem. Pharm. Bull.* **29**, 2753 (1981).
15. Quinteiro M., Seoane C., Soto J. L.: *J. Heterocycl. Chem.* **15**, 57 (1978).
16. Marchalín Š., Trška P., Kuthan J.: *This Journal* **49**, 421 (1984).
17. Long L. M., Henze H. R.: *J. Amer. Chem. Soc.* **63**, 1939 (1941).

Translated by M. Tichý.