CYCLOCONDENSATION REACTIONS OF 4-R-BENZYLIDENE-4-PHENYLBENZOYLACETONITRILES WITH CYCLOALKANONES*

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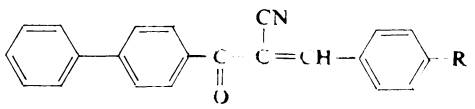
Cyclocondensation of 4-R-benzylidene-4-phenylbenzoylacetonitriles *I* with cycloalkanones *II* in the presence of ammonium acetate gives 4-aryl-2-(4-biphenylyl)-3-cyanocycloalkeno[*b*]pyridines *IV*–*VI*. A detailed study of the reaction course of cyclohexanone (*IIa*) with the ketonitriles *Ia*–*Ij* has shown that the bicyclic 1,4-dihydropyridine derivatives *III*, which easily undergo oxidation with air oxygen, are the intermediates in the formation of the heteroaromatic compounds *IV*. A mechanism is suggested for the reaction, and the dependence is discussed between structure of the synthetized compounds *III*–*VI* and their spectral properties.

Several procedures were developed for synthesis of cycloalkeno[*b*]pyridines, *viz.* cyclization reactions of compounds which contain no pyridine ring[1–3], ring fusion of 2,3-disubstituted pyridines[4,5], or reduction of quinoline derivatives[6–8]. Recently, the ketonitriles type *I* were also used in synthesis of 5-amino-3-cyanofurans[9], unsymmetrically substituted 3,5-dicyano-1,4-dihydropyridines[10], and 2-amino-4*H*-pyrans[10–12]. The present communication deals with study of the cyclocondensation reactions of β-ketonitriles *I* with cycloalkanones *II* and ammonium acetate as a new



Ia, R = NO_2
Ib, R = H
Ic, R = OC_2H_5
Id, R = $N(C_2H_5)_2$
Ie, R = OCH_3
If, R = F
Ig, R = Cl
Ih, R = CH_3
Ii, R = i-C_3H_7
Ij, R = $NHCOCH_3$

potential method of preparation of cycloalkeno[*b*]pyridines. 4-Aryl-2-(4-biphenylyl)-3-cyanocycloalkeno[*b*]pyridines *V* and *VI* were prepared in the yields of 50–80% (Table I) by the cyclocondensation of β-ketonitriles *Ia*–*Id* with cycloalkanones *IIb*

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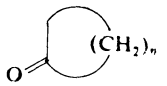
TABLE I

4-Aryl-2-(4-biphenylyl)-3-cyanocycloalkeno[*b*]pyridines *IV*– *VI*

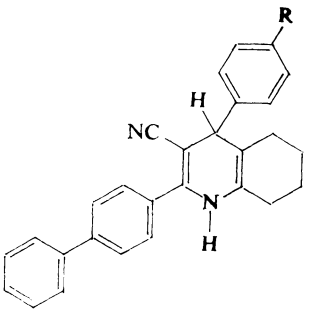
Compound (R)	Yield, % (procedure)	M.p., °C[a]	Formula (mol. mass)	Calculated/Found		
				% C	% H	% N
IVb	~100	166–169[b]	$C_{28}H_{22}N_2$	87·00	5·74	7·25
(H)	(*B*)		(386·5)	86·72	5·71	7·18
IVc	66	217–220	$C_{30}H_{26}N_2O$	83·68	6·10	6·51
(OC_2H_5)	(*A*)		(430·6)	83·89	6·18	6·42
IVd	69	169–172[c]	$C_{32}H_{31}N_3$	83·98	6·84	9·18
($N(C_2H_5)_2$)	(*A*)		(457·7)	84·01	6·96	8·95
IVe	~100	199–201	$C_{29}H_{24}N_2O$	83·61	5·82	6·73
(OCH_3)	(*B*)		(416·6)	83·13	5·89	6·64
IVf	~100	201–203	$C_{28}H_{21}FN_2$	83·13	5·24	6·93
(F)	(*B*)		(404·5)	82·89	5·34	6·96
IVg	68	194–196[c]	$C_{28}H_{21}ClN_2$[d]	79·88	5·04	6·66
(Cl)	(*A*)		(421.·0)	79·59	5·05	6·63
IVh	55	192–194	$C_{29}H_{24}N_2$	86·95	6·05	7·00
(CH_3)	(*A*)		(400·5)	86·87	6·26	6·89
IVi	69	182–183	$C_{31}H_{28}N_2$	86·86	6·60	6·54
(i-C_3H_7)	(*A*)		(428·6)	87·08	6·79	6·48
IVj	86	288–290	$C_{30}H_{25}N_3O$	81·23	5·69	9·48
($NHCOCH_3$)	(*A*)		(443·6)	81·03	5·58	9·39
Va	80	242–244	$C_{29}H_{23}N_3O_2$	78·17	5·21	9·43
(NO_2)	(*A*)		(445·6)	78·16	5·31	9·17
Vb	62	187–188	$C_{29}H_{24}N_2$	86·95	6·05	7·00
(H)	(*A*)		(400·5)	86·93	6·25	6·94
Vc	51	197–199	$C_{31}H_{28}N_2O$	83·74	6·36	6·30
(OC_2H_5)	(*A*)		(444·6)	83·63	6·33	6·26
Vd	48	172–173	$C_{33}H_{33}N_3$	84·02	7·07	8·91
($N(C_2H_5)_2$)	(*A*)		(471·7)	83·98	7·06	8·89
VIa	62	225–227	$C_{30}H_{25}N_3O_2$	78·40	5·49	9·15
(NO_2)	(*A*)		(459·6)	78·28	5·40	9·08
VIb	50	172–174[b]	$C_{30}H_{26}N_2$	86·91	6·33	6·76
(H)	(*A*)		(414·6)	86·73	6·25	6·51
VIc	74	176–179[c]	$C_{32}H_{30}N_2O$	83·80	6·61	6·11
(OC_2H_5)	(*A*)		(458·6)	83·52	6·48	6·39
VId	71	223–225	$C_{34}H_{35}N_3$	84·07	7·28	8·65
($N(C_2H_5)_2$)	(*A*)		(485·7)	84·17	7·55	8·23

[a] Crystallized from ethanol–benzene; [b] crystallized from ethanol; [c] crystallized from n-hexane–benzene; [d] calculated: 8·42% Cl; found: 8·47% Cl.

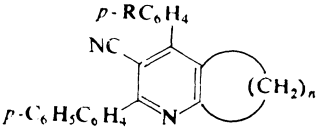
and *IIc* in the presence of ammonium acetate (procedure *A*). The course of this reaction was studied in detail with cyclohexanone (*IIa*) as a model substrate and ketonitriles *Ia–Ij*. From the reactions of compounds *Ic*, *Id*, and *Ig–Ij* (R = OC_2H_5, $N(C_2H_5)_2$, Cl, CH_3, i-C_3H_7, and $NHCOCH_3$) we isolated as the reaction products the cycloalkeno[*b*]pyridines *IVc*, *IVd*, and *IVg–IVj*. On the contrary, if the reaction



IIa, *n* = 4
IIb, *n* = 5
IIc, *n* = 6



IIIa–c, *IIIe*, *IIIf*

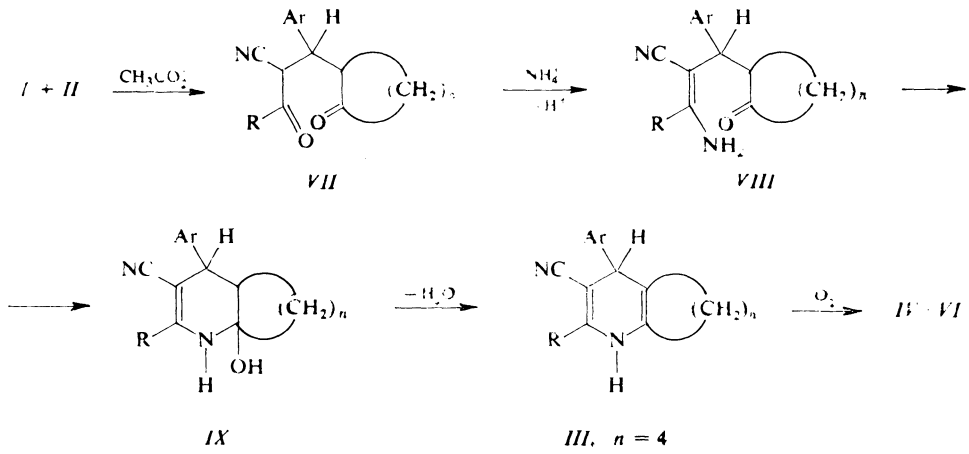


IVb–j, n = 4
Va–d, n = 5
VIa–d, n = 6

was carried out with compounds *Ia*, *Ib*, *Ie*, and *If* (R = NO_2, H, OCH_3, F) under the same conditions, then the intermediates separated which were identified as 4-aryl-2-(4-biphenylyl)-1,4-dihydro-3-cyanocyclohexeno[*b*]pyridines *IIIa*, *IIIb*, *IIIe*, and *IIIf* (Table II). The bicyclic 1,4-dihydrocyclohexeno[*b*]pyridine derivatives *III* are little stable in solution and undergo easily oxidation with air oxygen. The presumption that the 1,4-dihydro derivatives *III* represent the intermediates in the formation of the cycloalkeno[*b*]pyridines *IV* was verified by quantitative oxidation of benzenic solution of compounds *IIIb*, *IIIe*, and *IIIf* with air oxygen giving the pyridines *IVb*, *IVe*, and *IVf*, resp. (procedure *B*, Table I). When the reaction of ketonitrile *Ic* (R = OC_2H_5) with cyclohexanone (*IIa*) was carried out with exclusion of air, the 1,4-dihydro derivative *IIIc* was isolated which underwent aromatization to compound *IVc* on standing (in benzene solution) in air. The given experiments also show that dehydrogenation of the compounds *III* by other compounds present in the reaction mixture plays a minimum role.

Scheme 1 gives probable mechanism of formation of the substituted cycloalkeno-[*b*]pyridines *IV–VI*. Presumably, the first reaction phase forms the 1,5-diketone *VII* which could give the acyclic enaminonitrile *VIII* on action of ammonia. The

ketonitriles *I* react with cycloalkanones *II* in the presence of ammonium acetate presumably by Michael addition to give the adducts *VII*, whereas the reaction catalyzed with piperidine[13] gives the condensation products *X*. The Knoevenagel condensation producing the compounds type *X* would exclude the possibility of formation of compounds *IV*–*VI*. The driving force of the reaction of 1,5-diketone *VII* with ammonia could consist in the formation of the conjugated enaminonitrile



SCHEME 1 (R = p-$C_6H_5C_6H_4$)

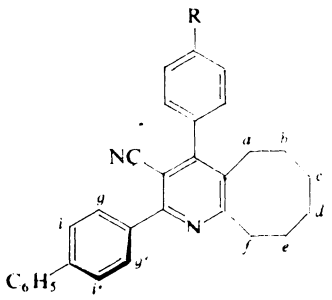
TABLE II

4-Aryl-2-(biphenylyl)-1,4-dihydro-3-cyanocyclohexeno[*b*]pyridines *III*

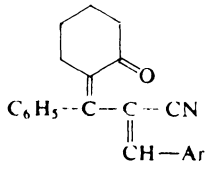
Compound (yield, %)	R	M.p., °C (solvent)	Formula (mol. mass)	Calculated/Found		
				% C	% H	% N
IIIa	NO_2	196–199	$C_{28}H_{23}N_3O_2$	77·57	5·36	9·69
(81)		(n-C_6H_{14}–C_6H_6)	(433·5)	77·59	5·45	9·81
IIIb	H	192–195	$C_{28}H_{24}N_2$	86·55	6·24	7·21
(70)		(C_2H_5OH)	(388·5)	86·31	6·05	7·06
IIIe	OCH_3	228–230	$C_{29}H_{26}N_2O$	83·21	6·27	6·69
(81)		(C_2H_5OH–C_6H_6)	(418·6)	83·17	6·47	6·72
IIIf	F	182–184	$C_{28}H_{23}FN_2$[a]	82·72	5·71	6·89
(62)		(n-C_6H_{14}–C_6H_6)	(406·5)	83·07	5·81	6·77

[a] Calculated: 4·67% F; found: 5·20% F.

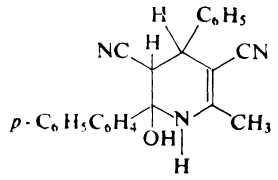
grouping in compound *VIII* which is obviously energetically preferred to the primary enamine of the cycloalkane section of the molecule. To support this presumption, the reaction of 4-phenylbenzoylacetonitrile with ammonium acetate was carried out in methanol, *i.e.* under the conditions of the above-mentioned cyclocondensation reactions, and it gave 3-amino-3-(4-biphenylyl)propenenitrile (*XI*) in the yield of 86%. In addition, the starting ketonitriles *I* evidently afforded with ammonium acetate no imino derivatives as it was proved in the cases of *Ib* and *Ie*. Intramolecular cyclization of the intermediate *VIII* could explain the formation of the bicyclic derivative *IX* which could give 1,4-dihydropyridine *III* on elimination of water. The cyclic Michael adduct *XII* analogous to the intermediate *IX* was trapped in the reaction of ketonitrile *Ib* with 3-amino-2-butenenitrile in basic medium[10], this compound being easily dehydrated in acid medium to give 2-(4-bi-



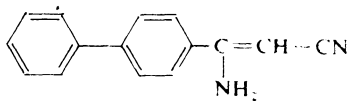
IV, *b*=*c* and *d*=*e*
V, *c*=*d*
VI



X



XII



XI

phenylyl)-3,5-dicyano-4-phenyl-1,4-dihydropyridine[10]. If the reaction was not carried out under inert atmosphere, then the 1,4-dihydropyridine derivatives type *III* could be oxidized with air to the final products *IV–VI*.

The infrared spectra of bicyclic 1,4-dihydropyridines *III* (see Table III) agree with the infrared characteristics of 1,4-dihydropyridines[14,15] and exhibit the absorption maxima of stretching vibrations of the groups C≡N, N—H, and methylene groups of cyclohexene ring (2 861 – 2 988 cm^{-1}). In the region 1 500 – 1 700 cm^{-1} there is an overlapping of the bands of vibrations of multiple bonds of 1,4-dihydropyridine skeleton (C=C—N—C=C) (ref.[14]) with those of the stretching vibrations $\nu(C{=}C)_{arom}$. The position of the absorption maximum at 1 700 cm^{-1} is characteristical for the compound type *III* and is not observed with the pyridines *IV–VI*. The stretching vibrations of C≡N groups (as expected[14,15]) are shifted to lower

TABLE III

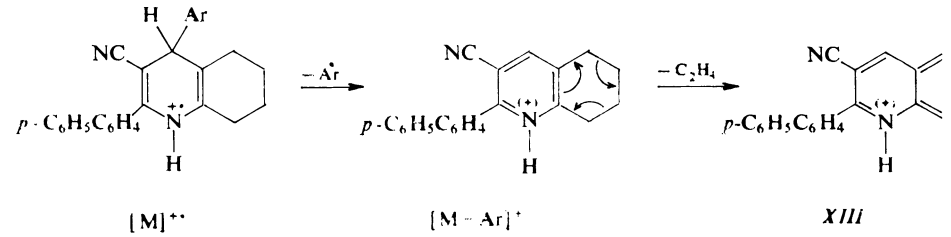
UV and IR spectra of 4-aryl-2-(4-biphenylyl)-1,4-dihydro-3-cyanocyclohexeno[*b*]pyridines *III*

Compound	UV spectrum[a]		IR spectrum ($CHCl_3$)					
	λ_{max}	log ε	ν(N—H)	ν(=C—H)	ν(C—H)	ν(C≡N)	ν(C=C) and ν(N—C=C)	
IIIa[b]	206	4·66	3 445 m	3 012 m	2 948 m	2 198 m	1 700 w	1 560 w
	245	4·21			2 868 w		1 609 m	1 526 s
	282	4·49			2 842 w		1 578 w	1 486 s
IIIb	206	4·75	3 442 m	3 014 m	2 940 m	2 195 s	1 700 w	1 523 w
	276	4·44			2 888 w		1 618 m	1 486 s
	357	3·80			2 840 w		1 609 m	
IIIc	206	4·67	3 449 m	3 018 m	2 988 w	2 197 s	1 700 w	1 542 w
	218 i	4·48			2 942 m		1 612 s	1 511 s
	279	4·45			2 890 w		1 585 w	1 486 s
	354	3·76			2 865 w		1 560 w	
IIIe	206	4·67	3 448 m	3 016 m	2 941 m	2 197 s	1 702 w	1 512 s
	243	4·18			2 892 w		1 612 m	1 486 s
	278	4·43			2 868 w		1 585 w	
	345	4·26			2 844 m		1 542 w	
IIIf	207	4·56	3 450 m	3 020 m	2 950 m	2 200 s	1 702 w	1 510 s
	245 i	4·07			2 892 w		1 621 m	1 486 s
	277	4·38			2 872 w		1 608 m	
	340	3·45			2 848 w		1 585 w	

[a] Concentration 8 . 10^{-6} mol l^{-1}, ethanol; [b] the absorption band 1 355 s $\nu_s(NO_2)$ was identified in IR spectrum of compound *IIIa*.

frequences in the bicyclic dihydro derivatives *III* as compared with the pyridines *IV–VI*. The infrared spectra of the cycloalkeno[*b*]pyridines *IV–VI* (Table IV) exhibit the absorption maxima of pyridine ring at 1 600 cm^{-1}, those of C≡N group and cycloalkene ring.

The ^1H NMR spectra agree with the structure of compounds *III–VI* (Tables V–VII). The signals of methylene groups of cycloalkene rings of compounds *IV–VI* were resolved by decoupling of the resonance signals in the model compound *VIb*. The aromatization of compounds *III* to *IV* results in a down-field shift of the proton signals of the cycloalkene ring, which is especially marked with the protons H_a and H_f. When comparing the ^1H NMR spectra of compounds *IV–VI* with those of the 1,4-dihydro derivatives *III* in the region of signals of aromatic protons (7·0–8·0δ), we can observe, besides a complex multiplet, also a characteristically localized doublet at 7·63–7·66δ which is found in all the compounds of the series *IV–VI*. This signal with the integral intensity corresponding to two protons was assigned to the *ortho* protons H_g and H_g, in biphenyl. The existence of this signal can be explained most simply by mutual approximately perpendicular conformation of the pyridine ring and the benzene ring bound to 2 position of the pyridine skeleton (as given in formulas *IV–VI*). In this conformation the protons H_g and H_g, become chemically equivalent, and the conjugation of the biphenyl with pyridine is at its minimum. The absence of this signal in 1,4-dihydropyridines *III* indicates a greater conformational coplanarity and, hence, greater conjugation of the biphenyl with 1,4-dihydropyridine skeleton, which is shown in formula *III*. With the compounds *III* we studied the fragmentation of molecule *IIIa* caused by the electron impact at 70 eV (Scheme 2). The splitting



SCHEME 2 (Ar = *p*-$CH_3OC_6H_4$)

off of the substituent from $C_{(4)}$ atom with formation of the ionic species *m/z* 311 $[M-Ar]^+$, which represents the basic peak, is a characteristical fragmentation process of 4-substituted 1,4-dihydropyridines[10,16,17]. The retro-Diels–Alder splitting of the cyclohexene ring in the $[M-Ar]^+$ ion produces the cation *XIII*. The most intensive ions in the mass spectra of the cycloalkeno[*b*]pyridines *IVc* and *Vb* are the molecular ions $[M]^{+\cdot}$ and $[M-1]^+$, respectively. Further fragmentation occurs preferably at the least stable cycloalkene ring.

TABLE IV

UV and IR spectra of the cycloalkeno[*b*]pyridines *IV*— *VI*

Compound	UV spectrum[a]		IR spectrum ($CHCl_3$)				
	λ_{max}	log ε	ν(=C—H)	ν(C—H)	ν(C≡N)	ν(C=C) and ν(C=N)	
IVb	206	4·77	3 020 m	2 956 m	2 235 m	1 614 s	1 542 m
	238 i	4·41		2 878 w		1 578 w	1 516 s
	289	4·48		2 852 w		1 566 w	1 492 m
IVc	207	4·69	3 018 m	2 988 m	2 228 m	1 614 s	1 542 s
	218 i	4·58		2 950 s		1 577 w	1 515 s
	239	4·19		2 876 w		1 565 w	1 490 m
	288	4·53					
IVd	207	4·71	3 020 w	2 984 m	2 229 m	1 614 s	1 520 s
	242	4·25		2 950 m		1 566 w	1 491 w
	269	4·39		2 880 w			
	289	4·47					
	362	4·04					
IVe	207	4·72	3 018 m	2 950 m	2 225 m	1 614 s	1 534 m
	217 i	4·61		2 878 w		1 578 w	1 515 s
	235	4·22		2 846 w		1 566 w	1 490 w
	287	4·54					
IVf	207	4·73	3 014 w	2 950 m	2 222 m	1 611 m	1 512 s
	288	4·44		2 870 w		1 565 w	1 490 w
						1 546 m	
IVg	207	4·73	3 020 m	2 958 s	2 236 m	1 610 w	1 545 s
	218 i	4·60		2 878 w		1 602 m	1 498 s
	238 i	4·29				1 566 m	
	287	4·49					
IVh	207	4·86	3 020 m	2 956 s	2 229 s	1 614 m	1 544 s
	218 i	4·70		2 878 m		1 603 w	1 518 s
	234 i	4·36				1 567 m	1 492 m
	285	4·55					
IVi	208	4·70	3 020 m	2 972 s	2 230 s	1 614 m	1 545 s
	217 i	4·56		2 956 s		1 603 w	1 514 m
	236	4·25		2 880 m		1 566 m	1 492 m
	286	4·50					
IVj[b]	206	4·75	3 018 m	2 950 m	2 222 m	1 612 w	1 541 m
	218 i	4·54		2 872 w		1 600 w	1 518 s
	240	4·41				1 592 w	1 490 m
	289	4·57				1 560 w	
Va[c]	209	4·61	3 020 m	2 970 w	2 229 m	1 605 s	1 527 s
	219 i	4·48		2 938 s		1 566 m	1 496 w
	244	4·25		2 862 m		1 548 s	1 488 m
	289	4·54					

TABLE IV
(*Continued*)

Compound	UV spectrum[a]		IR spectrum ($CHCl_3$)				
	λ_{max}	log ε	ν(=C—H)	ν(C—H)	ν(C≡N)	ν(C=C) and ν(C=N)	
Vb	207	4·66	3 072 w	2 978 w	2 228 s	1 613 w	1 546 s
	218 i	4·47	3 020 m	2 940 s		1 604 w	1 492 s
	242	4·21		2 862 m		1 568 s	
	290	4·46					
Vc	209	4·61	3 018 w	2 992 m	2 230 m	1 614 s	1 514 s
	219 i	4·48		2 940 s		1 566 w	1 490 m
	244	4·24		2 863 m		1 542 s	1 481 m
	289	4·54					
Vd	208	4·69	3 019 w	2 980 m	2 228 m	1 612 s	1 520 s
	244	4·27		2 938 s		1 566 w	1 490 m
	269	4·46		2 862 w			
	291	4·54					
	349	3·93					
VIa[d]	207	4·80	3 018 w	2 936 m	2 224 m	1 603 m	1 526 s
	218 i	4·64		2 862 w		1 565 w	1 489 w
	244	4·33				1 542 m	
	288	4·54					
VIb	208	4·64	3 062 w	2 932 s	2 223 m	1 610 w	1 544 s
	218 i	4·48	3 016 m	2 860 m		1 602 w	1 490 s
	244	3·96				1 566 m	
	291	4·47					
	369	3·34					
VIc	207	4·82	3 020 w	2 990 w	2 230 m	1 615 s	1 515 s
	218 i	4·72		2 939 s		1 576 w	1 490 m
	243	4·13		2 864 m		1 566 w	1 481 m
	289	4·59				1 540 m	
VId[e]	207	—	3 018 w	2 990 m	2 230 m	1 612 s	1 519 s
	218 i	—		2 940 m		1 562 w	1 490 m
	244	—		2 864 w			
	269	—					
	289	—					
	357	—					

[a] Concentration $8 \cdot 10^{-6}$ mol l^{-1}, ethanol; [b] the following absorption bands were identified in IR spectrum of compound *IVj*: 3 440 m ν(N—H) and 1 698 s ν(C=O); [c] the absorption band 1 352 s $\nu_s(NO_2)$ was found in IR spectrum of compound *Va*; [d] the absorption band 1 351 s $\nu_s(NO_2)$ was found in IR spectrum of compound *VIa*; [e] measured as saturated solution in ethanol.

TABLE V

^{1}H NMR Spectral characteristics of 1,4-dihydrocyclohexeno[*b*]pyridines *III*

Compound	Chemical shifts		δ_H, ppm ($^2HCCl_3$, 35°C)[a]			
	$-(CH_2)_3-$	H—C(8)	H—C(4)	H—N	H_{arom}	R
IIIa	1·42—1·94 m	2·05—2·30 m	4·24 s	5·54 br. s	7·25—7·80 m 8·20 d (H_{ortho})	—
IIIb	1·40—1·90 m	1·96—2·22 m	4·07 s	5·54 br. s	7·20—7·76 m	—
IIIc	1·50—1·96 m	2·00—2·30 m	4·08 s	5·44 br. s	7·15—7·85 m 6·86 d (H_{ortho})	1·41 t 4·04 q
IIIe	1·50—1·94 m	2·00—2·26 m	4·10 s	5·38 br. s	7·15—7·75 m 6·88 d (H_{ortho})	3·82 s
IIIf	1·40—1·94 m	1·97—2·22 m	4·07 s	5·40 br. s	6·87—7·73 m	—

[a] Tetramethylsilane as the internal standard.

TABLE VI

^{1}H NMR Chemical shifts of cyclohexeno[*b*]pyridines *IV*. The data in ppm related to tetramethylsilane ($^2HCCl_3$, 35°C)

Compound	H-a[a]	H-b, e[a]	H-f[a]	H-g, g′	H-i, i′	H_{arom}	R
IVb	2·51 m	1·82 m	3·08 m	7·93 d	7·66 d	7·18—7·60 m	—
IVc	2·52 m	1·81 m	3·07 m	7·92 d	7·65 d	7·10—7·58 m 6·96 d (H_{ortho})	1·43 t 4·04 q
IVd	2·57 m	1·80 m	3·02 m	7·91 d	7·63 d	7·25—7·55 m 7·10 d (H_{meta}) 6·67 d (H_{ortho})	1·19 t 3·36 q
IVe	2·54 m	1·84 m	3·08 m	7·93 d	7·65 d	7·17—7·60 m 7·03 d (H_{ortho})	3·88 s
IVf	2·50 m	1·84 m	3·10 m	7·94 d	7·68 d	7·14—7·61 m	—
IVg	2·52 m	1·82 m	3·08 m	7·93 d	7·66 d	7·18—7·59 m	—
IVh	2·50 m	1·80 m	3·07 m	7·93 d	7·66 d	7·12—7·57 m	2·40 s
IVi	2·49 m	1·80 m	3·05 m	7·92 d	7·64 d	7·14—7·58 m	1·29 d 2·94 m
IVj	2·49 m	1·82 m	3·06 m	7·90 d	7·65 d	7·17—7·59 m	2·08 s 8·14 br. s

[a] The centres of symmetrical multiplets.

TABLE VII

^{1}H NMR Spectra of cycloalkeno[*b*]pyridines *V* and *VI*. The data in ppm related to tetramethylsilane ($^2HCCl_3$, 35°C)

Compound	H-a[a]	H-b[a]	H-c, d[a]	H-e[a]	H-f[a]	H-g, g′	H-i, i′	H_{arom}	R
Va	2·61 m	1·85 m	1·58 m	1·85 m	3·22 m	7·97 d	7·64 d	7·17—7·58 m 8·31 m (H_{ortho})	—
Vb	2·62 m	1·81 m	1·58 m	1·81 m	3·19 m	7·96 d	7·66 d	7·14—7·61 m	—
Vc	2·66 m	1·82 m	1·59 m	1·82 m	3·20 m	7·95 d	7·65 d	7·26—7·56 m 7·16 d (H_{meta}) 6·94 d (H_{ortho})	1·42 t 4·04 q
Vd	2·75 m	1·83 m	1·59 m	1·83 m	3·20 m	7·95 d	7·65 d	7·25—7·57 m 7·10 d (H_{meta}) 6·69 d (H_{ortho})	1·20 t 3·37 q
VIa	2·65 m	1·45 m	1·45 m	1·91 m	3·15 m	7·97 d	7·68 d	7·25—7·58 m 8·34 d (H_{ortho})	
VIb	2·68 m	1·43 m	1·43 m	1·90 m	3·13 m	8·00 d	7·68 d	7·20—7·65 m	—
VIc	2·70 m	1·44 m	1·44 m	1·91 m	3·11 m	7·96 d	7·66 d	7·28—7·62 m 7·16 d (H_{meta}) 6·95 d (H_{ortho})	1·44 t 4·04 q
VId	2·76 m	1·45 m	1·45 m	1·90 m	3·11 m	7·98 d	7·67 d	7·26—7·62 m 7·10 d (H_{meta}) 6·70 d (H_{ortho})	1·20 t 3·37 q

[a] The centres of symmetrical multiplets.

The band localized at 340–357 nm (log ε 3·45–4·26) in the UV absorption spectra of the bicyclic 1,4-dihydropyridines *III* (Table III) represents a characteristical absorption band of the 1,4-dihydropyridine chromophore[14,15], corresponding to the $\pi \rightarrow \pi^*$ transition in accordance with structure of the compounds *III*. Cycloalkeno-[*b*]pyridines *IV–VI* (Table IV) exhibit the absorption bands at 206–209 nm (log ε 4·61–4·86), 234–244 nm (log ε 3·96 –4·41), and 285–291 m (log ε 4·44–4·59). In the case of the compounds *IVd*, *Vd*, and *VId* (R = $N(C_2H_5)_2$) we observed an absorption band at 349–362 nm (log ε 3·93–4·04) which disappeared when the spectrum was remeasured in acidic medium (2M hydrochloric acid in ethanol). This band is probably connected with the longest-wave transition of the chromophore of the non-protonated form. The protonation takes place preferably at the electron pair of nitrogen atom of diethylamino group, which excludes this electron pair from conjugation, and the longest-wave band is shifted hypsochromically as compared with the non-protonated form. Under the measurement conditions the protonation of pyridine nitrogen atom is also possible, so the observed spectrum could be assigned to the diprotonated form of the molecules *IVd*, *Vd*, and *VId*. The protonation of pyridine ring causes a bathochromical shift of the aromatic bands by $\Delta\lambda$ = 25 to 37 nm and decrease in their intensities by $\Delta \log \varepsilon = -(0{\cdot}12$ to $0{\cdot}29)$ as compared with the spectra measured in ethanol. An analogous shift of aromatic absorption bands was observed in UV absorption spectra of the compounds *Vc* and *VIc* which can only give the mono-protonated forms. These relations are clearly seen in Fig. 1 (for the pyridine *IVd*).

EXPERIMENTAL

The temperature data are not corrected. The melting temperatures were determined with a Boetius apparatus. The following apparatus was used for the spectral measurements: Perkin–Elmer 325 (IR), Carl Zeiss, Jena Specord UV VIS (UV), Varian XL-100, Tesla BS 567 (^{1}H NMR), and LKB 9000 (MS, 70 eV).

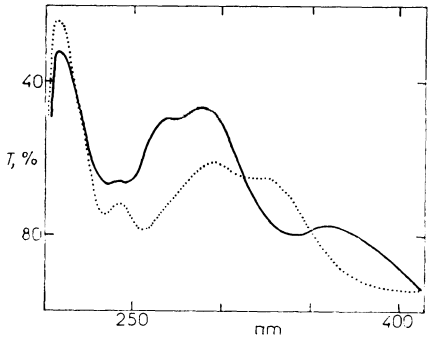


FIG. 1

Electronic spectrum of 2-(4-biphenylyl)-4-(4-diethylaminophenyl)-3-cyanocyclohexeno-[*b*]pyridine (*IVd*) for *c.* $1 \cdot 10^{-5}$ mol l^{-1}. Full curve ethanol, dotted curve hydrogen chloride in ethanol, 2 mol l^{-1}

The synthesis of ketonitriles *I* and 4-phenylbenzoylacetonitrile is described in our previous communication[18]. Purity of the synthetized compounds was checked by thin layer chromatography using Silufol plates (Lachema, Brno) and detection with UV light and iodine vapour.

4-Aryl-2-(4-biphenylyl)-3-cyanocycloalkeno[*b*]pyridines *IV*—*VI*

A) Mixture of 1·5 mmol ketonitrile *I*, 1·5 mmol cycloalkanone *II*, and 2 mmol ammonium acetate in 7 ml ethanol was boiled 8 h and left to stand for several days. The separated crystalline solid was collected by suction, washed with little water, with ethanol, and recrystallized from a suitable solvent. In the case of the pyridine *IVj* the reaction was carried out in acetonitrile. In the cases of the pyridines *IVd*, *IVj*, *Vb*, and *VIa*, which did not crystallize from the solutions, the solvent was distilled off under reduced pressure. The viscous residue was transferred on a ceramic plate and left to stand in n-hexane vapours until it crystallized.

B) Solution of 100 mg of the respective 1,4-dihydropyridine *III* in benzene was left to stand in air for several days. Benzene was distilled off under reduced pressure, and the pyridines *IVb*, *IVc*, *IVe*, and *IVf* were crystallized from suitable solvents. The yields of the cycloalkeno[*b*]pyridines *IV*—*VI* obtained, the solvents used for crystallizations, the melting temperatures and analytical data are given in Table I.

4-Aryl-2-(4-biphenylyl)-1,4-dihydro-3-cyanocyclohexeno[*b*]pyridines *IIIa*, *IIIb*, *IIIe*, and *IIIf*

Mixture of 1·5 mmol of the respective ketonitrile *I*, 1·5 mmol cyclohexanone (*IIa*), and 1·5 mmol ammonium acetate in 7 ml ethanol was boiled 8 h, the first 5 min of the heating already being accompanied by separation of a precipitate. The mixture was left to stand overnight, the product *III* was collected by suction, washed with little water, with ethanol, and recrystallized from a suitable solvent with exclusion of air. The synthetized derivatives *III* are listed in Table II.

2-(4-Biphenylyl)-1,4-dihydro-4-(4-ethoxyphenyl)-3-cyanocyclohexeno[*b*]pyridine (*IIIc*)

Mixture of 0·5 g ketonitrile *Ic*, 0·14 g cyclohexanone (*IIa*), and 0·11 g ammonium acetate in 7 ml ethanol was boiled 8 h under dry argon. After 30 min of heating a precipitate began to separate which was collected by suction, washed with ethanol, and crystallized from ethanol–benzene (1 : 1) mixture with exclusion of air. Yield 0·5 g (86%), m.p. 201—204°C. For $C_{30}H_{28}N_2O$ (432·6) calculated: 83·29% C, 6·54% H, 6·48% N; found: 82·96% C, 6·51% H, 6·26% N.

3-Amino-3-(4-biphenylyl)propenenitrile (*XI*)

Mixture of 0·7 g 4-phenylbenzoylacetonitrile and 0·24 g ammonium acetate in 10 ml methanol was boiled 6 h and left to stand overnight. The separated solid was collected by suction, washed with little water, with methanol, and recrystallized from 1,2-dimethoxyethane. Yield 0·6 g (86%), m.p. 188—190°C (ref.[19], m.p. 188—190°C). The identity of the product *XI* was confirmed by comparison of its spectral characteristics with those of the enaminonitrile *XI* prepared by condensation of 4-cyanobiphenyl with acetonitrile[17].

Mass Spectra (ions and relative %)

IIIe: 419 (4), 418 (11, $[M]^{+\cdot}$), 417 (6), 313 (4), 312 (28), 311 (100, $[M-CH_3OC_6H_4]^+$), 310 (5), 309 (4), 283 (4), 265 (3), 209 (1, $[M]^{2+}$), 153 (3), 152 (6), 151 (2), 115 (3), 92 (4), 91 (3), 79 (3), 78 (24), 77 (16).

IVe: 418 (5), 417 (22), 416 (100, $[M]^{+\bullet}$), 415 (82), 402 (8), 401 (17), 387 (4), 386 (7), 385 (15), 373 (7), 372 (7), 371 (7), 357 (5), 345 (6), 344 (5), 343 (4), 208 (3, $[M]^{2+}$), 179 (3), 178 (5), 177 (4), 176 (2), 169 (5), 165 (4), 164 (4), 153 (3), 152 (6), 151 (4), 114 (4), 91 (4), 78 (32). 77 (11), 76 (3).

Vb: 401 (13), 400 (65, $[M]^{+\bullet}$), 399 (100, $[M-1]^{+}$), 398 (3), 385 (3), 383 (2), 372 (3), 371 (7), 370 (2), 369 (4), 358 (3), 357 (3), 345 (2), 344 (3), 343 (2), 200 (1, $[M]^{2+}$), 179 (2), 178 (2), 165 (2), 153 (2), 152 (4), 151 (2), 115 (2), 91 (2), 78 (8), 77 (4), 71 (2), 69 (2).

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