ALKYLATION OF 2,4,4,6-TETRAPHENYL-1,4-DIHYDROPYRIDINE

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Received July 29, 1988
Accepted September 13, 1788

A series of photochromic N-methyl derivatives *IIIa*—*IIIh* was synthesized by alkylation of 1-sodio-2,4,4,6-tetraphenyl-1,4-dihydropyridine (*II*) in an inert atmosphere. On the other hand, the starting material *II* afforded products *IVa* and *IVb* in the presence of atmospheric oxygen. Mechanisms of acidobasic transformations of compounds *IVa* and *IVb* are discussed and spectral characteristics of new compounds are interpreted.

The 1-substituted 2,4,4,6-tetraphenyl-1,4-dihydropyridines *III* reveal noticeable optical properties. In our previous contribution[1] we described their preparation by cyclocondensation of 1,3,3,5-tetraphenyl-1,5-pentadione with N-substituted ammonium acetates. The 1-substituted 1,4-dihydropyridine derivatives can alternatively be obtained by treatment of strongly nucleophilic 1-alkali-metal salts of the appropriate heterocycles with alkylation reagents[2]. This paper describes the application of this procedure to 1-sodio-2,4,4,6-tetraphenyl-1,4-dihydropyridine (*II*).

As found, the solution of *II* in dimethylformamide can easily be prepared from the well accessible[1] 2,4,4,6-tetraphenyl-1,4-dihydropyridine (*I*) and sodium hydride in an inert atmosphere. Yields of alkyl derivatives *III* are quite high (87–96%) providing the alkyl chain of the halogen derivative was not branched. The yields however, strongly decreased with increasing bulkiness of the substituent. Thus, 2-propyl chloride furnished compound *IIIi* in only 2% yield, whilst tert-butyl chloride, trimethylsilyl and cyclohexyl chlorides did not alkylate at all; after work-up, starting material was quantitatively isolated from the mixture.

Physicochemical and spectral properties of newly synthesized compounds are listed in Table I. The proton signals at the aromatic ring in the ^{1}H NMR spectra of substances *IIIa*—*IIIh* (Table II, measured in deuteriochloroform solutions) were interpreted by analogy with our preceding paper[3]. Due to molecular symmetry, protons in positions 3 and 5, as well as equal protons at symmetric phenyl groups in positions 2, 6 and 4, 4 are isochronous. The most significant paramagnetic shift in compounds *IIIa*—*IIIg* showed signals of *ortho*-protons H-2b (for numbering cf. formula *III*), whilst the most shielded were found the *para*-protons H-4d. Due to the presence

Collect. Czech. Chem. Commun. (Vol. 54) (1989)

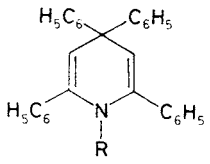
TABLE I

Physicochemical and spectral characteristics of compounds *IIIa*—*IIIh*

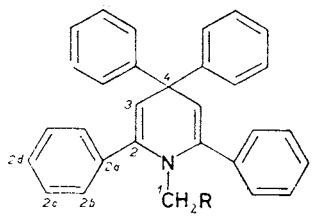
Compound R	M.p. (°C) Yield (%)	Formula (M.w.)	Calculated/Found			IR[a] $\tilde{\nu}$, cm^{-1}	UV, nm (log ε)
			% C	% H	% N		
IIIa	181—182	$C_{30}H_{35}N$	90·35	6·02	3·63	1 660	234·6(4·4)
H	96	(399·5)	90·27	6·10	3·54	1 600	288·0(3·8)
IIIb	152—154	$C_{31}Z_{27}N$	90·03	6·58	3·39	1 658	234·9(4·4)
CH_3	93	(413·6)	90·09	6·55	3·29	1 598	284·2(3·8)
IIIc	146—147	$C_{32}H_{29}N$	89·89	6·84	3·27	1 655	234·6(4·4)
C_2H_5	90	(427·6)	89·80	6·77	3·22	1 598	287·2(3·8)
IIId	107—109	$C_{33}H_{31}N$	89·75	8·08	3·17	1 655	236·0(4·4)
n-C_3H_7	87	(441·6)	89·70	7·09	3·10	1 597	288·5(3·8)
IIIe	134—136	$C_{32}H_{27}N$	90·31	6·39	3·29	1 659	232·9(4·4)
$CH{=}CH_2$	81	(425·6)	90·29	6·44	3·28	1 598	283·2(3·8)
IIIf	oil	$C_{41}H_{47}N$	88·92	8·55	2·53	1 658	235·5(4·3)
n-$C_{11}H_{23}$	90	(553·8)	88·84	8·61	2·51	1 599	288·5(3·7)
IIIg	174—176	$C_{36}H_{29}N$	90·91	6·15	2·94	1 657	237·3(4·4)
C_6H_5	87	(475·6)	90·98	6·21	3·08	1 598	284·0(3·8)
IIIh	190—192	$C_{43}H_{33}NO$	89·09	5·74	2·42	1 655	246·4(4·4)
p-$C_6H_5COC_6H_4$	80	(579·75)	89·12	5·80	2·51	1 599	—

[a] Dihydropyridine ring.

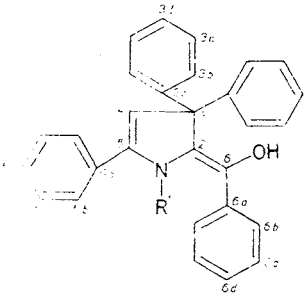
of a carbonyl group in compound *IIIh*, the most shielded were the *para*- and *meta*-protons at the benzoyl group in position 1. Similarly, carbon signals in the aromatic range of the ^{13}C NMR spectra of compounds *IIIa*–*IIIh* (Table III) were ascribed by analogy of substance *IIIa* with literature[3], where the assignment was backed by



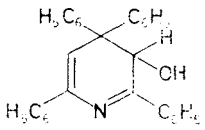
I, R = H
II, R = Na



IIIa, R = H
IIIb, R = CH_3
IIIc, R = C_2H_5
IIId, R = n-C_3H_7
IIIe, R = $CH{=}CH_2$
IIIf, R = n-$C_{11}H_{23}$
IIIg, R = C_6H_5
IIIh, R = p-$C_6H_5COC_6H_4$
IIIi, R = i-C_3H_7



IVc, R = H
IVb, R = CH_3



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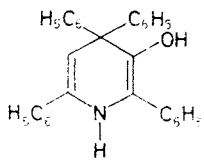


VI

COSYDQF, HETCOR2D and RELAY experiments. The IR spectra of chloroform solutions of *IIIa*–*IIIh* exhibited skeletal vibrations[4] of approximately equal medium intensity bands at 1 655–1 660 and 1 597–1 600 cm^{-1} of the dihydropyridine ring. The UV spectra of ethanolic solutions of *IIIa*–*IIIg* were characteristic of two absorption bands at 233–237 and 284–289 nm having a hypsochromic shift by 2–7 nm when contrasted with the not alkylated dihydropyridine *I*. Compound *IIIh* displayed only one maximum at 246 nm. All dihydropyridines *III* with exception of *IIIf*, which resisted attempts on crystallization, exhibited photochromism in crystalline state. Upon UV irradiation these compounds turned pink; this colouration disappeared more or less rapidly when stored in dark or on heating.

TABLE II

^{1}H NMR spectra of compounds *IIIa*—*IIIh*

Compound[a]	δ, ppm (^2J, Hz)							
	1	*2b*	*2c*	*2d*	*2d*	*4b*	*4c*	*4d*
IIIa	2·60 s	7·55 d (7·0)	7·37 t (7·3)	7·33 t (7·2)	5·27 s	7·29 d (7·9)	7·31 t (7·5)	7·16 t (6·6)
IIIb	3·12 q (7·0)[b]	7·58 d (6·8)	7·37 t (7·2)	7·33 t ([i])	5·34 s	7·28 d (8·2)	7·32 t ([i])	7·15 t (6·7)
IIIc	3·02 t (7·5)[c]	7·55 d (6·8)	7·37 t (7·2)	7·33 t ([i])	5·26 s	7·28 d (8·3)	7·31 t ([i])	7·15 t (6·9)
IIId	3·06 t (7·2)[d]	7·55 d (6·8)	7·37 t (7·1)	7·33 t ([i])	5·27 s	7·28 d ([i])	7·31 t ([i])	7·14 t (6·8)
IIIe	3·64 d (6·3)[e]	7·54 d (6·7)	7·36 t (6·9)	7·32 t ([i])	5·31 s	7·28 d (8·2)	7·30 t ([i])	7·15 t (6·8)
IIIf	3·06 t (7·3)[f]	7·55 d (6·9)	7·35 t (7·0)	7·32 t ([i])	5·27 s	7·27 d (8·1)	7·31 t ([i])	7·13 t (7·1)
IIIg	4·26 s[g]	7·55 d (6·8)	7·39 t (7·4)	7·33 t (7·1)	5·24 s	7·10 d ([i])	7·19 t (7·7)	7·09 t (7·0)
IIIh	4·21 s[h]	7·45 d (7·0)	7·36 t ([i])	7·33 t ([i])	5·19 s	7·22 d (7·8)	7·28 t (7·7)	7·07 t (7·5)

[a] For numbering hydrogen atoms see formula *III*; [b] signal of the methyl group is a triplet at δ 0·53 (^2J = 7·0 Hz); [c] further signals: 0·99 q, 2 H, ^2J = 7·4 Hz and 0·32 t, 3 H, ^2J = 7·4 Hz; [d] further signals: 0·95 q, 2 H, ^2J = 7·5 Hz, 0·72 q, 2 H, ^2J = 7·6 Hz and 0·39 t, 3 H, ^2J = = 7·3 Hz; [e] methine group appeared as a symmetric multiplet centered at δ 5·28, *cis*-proton at the vicinal methylene group is a doublet of a doublet at δ 4·69 (^2J = 10·2 Hz) and *trans*-proton a doublet of a doublet at δ 4·51 (^2J = 17·2 Hz); [f] further signals form a complex multiplet at δ 0·67—1·35, 23 H; [g] further signals: 6·58 d, 2 H (*ortho*), ^2J = 8·4 Hz, 6·89 t, 2 H (*meta*), ^2J = 7·8 Hz and 7·02 t, 1 H (*para*), ^2J = 7·4 Hz; [h] further signals: 6·56 d, 2 H, ^2J = 8·1 Hz, 6·98 d, 2 H, ^2J = 7·1 Hz, 7·56 d, 2 H, ^2J = 7·0 Hz, 6·94 t, 2 H, ^2J = 7·1 Hz, 7·67 t, 1 H, ^2J = = 8·1 Hz; [i] coupling constant is unreadable, multiplets overlap each other.

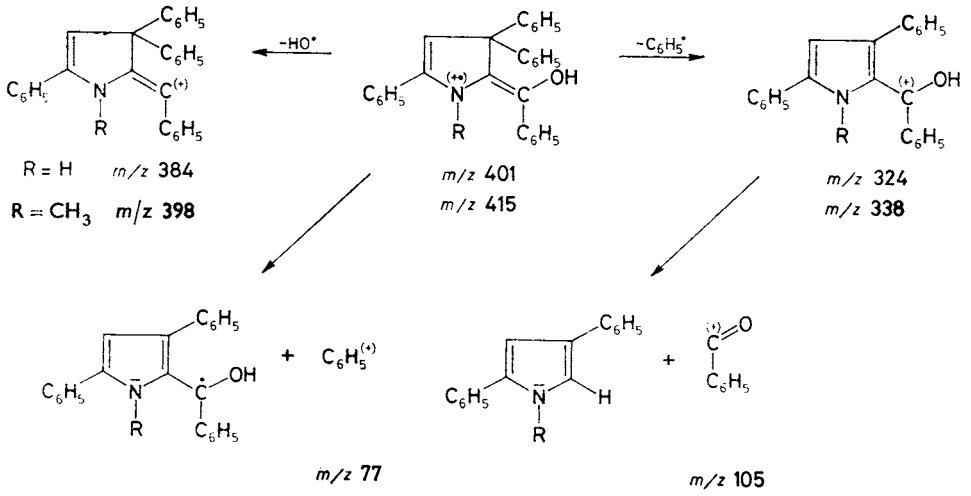
TABLE III

^{13}C NMR spectra of compounds *IIIa*—*IIIh* (δ, ppm)

Compound[a]	C-1	C-2	C-2a	C-2b	C-2c	C-2d	C-3	C-4	C-4a	C-4b	C-4c	C-4d
IIIa	38·28	143·33	138·02	128·00	128·28	128·00	112·32	49·44	151·41	127·87	128·15	125·54
IIIb	42·97[b]	142·00	138·14	128·05	128·27	128·05	114·39	49·37	151·53	127·94	128·13	125·49
IIIc	49·93[c]	142·93[c]	138·12	128·03	128·23	128·28	113·08	49·35	151·53	127·91	128·11	125·47
IIId	47·81[d]	142·41	138·06	128·06	128·20	127·89	113·33	49·30	151·53	128·01	128·11	125·45
IIIe	51·02[e]	142·11	137·99	128·02	128·24	127·98	114·10	49·37	151·23	128·00	128·20	125·52
IIIf	48·11[f]	142·43	138·12	128·08	128·20	127·80	113·15	49·32	151·56	128·02	128·10	125·45
IIIg	51·53[g]	141·93	138·04	128·08	128·33	128·00	114·14	49·33	151·19	127·97	128·21	125·26
IIIh	51·28[h]	141·70	137·70	128·03	128·25	128·05	114·72	49·15	151·14	127·94	128·19	125·47

[a] For numbering carbon atoms see formula *III*; [b] the methyl group signal appeared at δ 13·23; [c] further signals at δ 22·07 and 10·92; [d] further signals at δ 31·10, 19·55, and 13·49; [e] vinyl group signals at δ 134·49 and 116·67; [f] further signals at δ 31·93, 29·61, 29·59, 29·48, 29·33, 29·16, 29·04, 28·84, 26·35, 22·69, and 14·10; [g] aromatic ring carbons of the benzyl group at δ 138·28, 127·70, 126·91, and 128·17; [h] further signals at δ 196·17, 143·05, 137·87, 135·94, 132·13, 129·89, 129·78, 128·51, and 128·17.

As ascertained, the sodium salt *II* is extremely sensitive against oxidation with dioxygen at room temperature and therefore, it differs from the analogous 3,5-disubstituted salts[2]. Consequently, oxidation products were obtained after decomposition of the mixture when the 1,4-dihydro derivative *I* was not reacted with sodium hydride in an inert atmosphere. For oxidation products *IVa* and *IVb* structures were assigned on the basis of their molecular spectra keeping in mind that compound *IVa* showed a completely different properties from those of the isomer *V* described in literature[6] as an oxidation product of 1,4-dihydropyridine *I* with a singlet dioxygen. The alternative structure *VI* is also improbable, because it should be tautomeric with *V*, which was not the case with our compound *IVa*. The most intense ion species found in the mass spectra of *IVa* and *IVb* most probably generated via processes shown in Scheme 1. The specific ion species for both compounds originated by



SCHEME 1

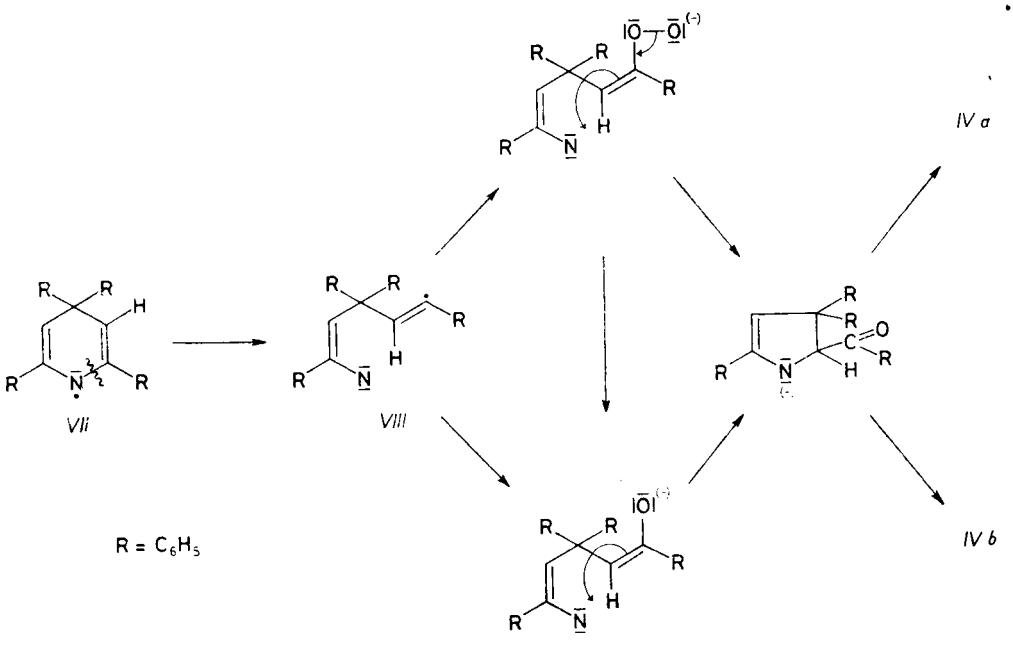
cleavage of phenyl and hydroxyl radicals; non specific seems to be the phenyl cation, the formation of which can be illustrated also by another pathway, and mainly from benzoyl cation. The latter ion species at *m/z* 105 forms a base peak the origination of which is very difficult to rationalize accepting structures *V* and *VI*. Also structure *IVa*, *IVb* are in line with their NMR spectra. Thus, the ^{1}H NMR spectrum of deuteriochloroform solution of compound *IVa* disclosed a broadened singlet at δ 8·39, which underwent a diamagnetic shift at higher temperature, and was attributed to the N-1 proton. Further signal, showing a diamagnetic shift at an elevated temperature, was the singlet at δ 2·91 ascribed to a hydroxyl proton at the exocyclic double bond. The proton signal in position 4 of the dihydropyrrole ring appeared as a doublet at δ 6·01 (^4J(H, H) = 3 Hz); this splitting is associated with the proton of the

N—H group through four bonds, this being in accord with an analogous splitting in the ^{1}H NMR spectrum of compound *I* as evidenced by a 2 D-COSY experiment[3].

The ^{1}H NMR spectrum of compound *IVb* recorded in deuteriochloroform solution exhibited a hydroxyl proton signal at δ 2·65, diamagnetically shifted at elevated temperature. Signal of an olefinic proton in position 4 was no longer splitted as with *IVa* and appeared as a singlet at δ 5·75. Due to molecular asymmetry of *IVa* and *IVb*, the ^{13}C NMR spectrum contained nine signals of tertiary bonded aromatic carbons, whilst only six signals in this region were seen with *IIIa*. The most pronounced shift showed, when compared with an analogous carbon atom in position 4 of compounds *III*, the quaternary carbon in position 3 resonating at δ 79·32 and 79·34 for compounds *IVa* and *IVb*, respectively. Interpretation of signals of the remaining carbon atoms in *IVa* and *IVb* was analogous with that of compounds *III* (cf. experimental section). The IR spectra of *IVa* and *IVb* measured in chloroform had indicative bands at 3 580 and 3 560 cm^{-1}, respectively, associated with vibrations of hydroxyl groups; the band at 3 458 cm^{-1} of compound *IVa* was ascribed to an N—H vibration.

The probable mechanism illustrating the formation of oxidation products of the salt *II* is presented in Scheme 2. An

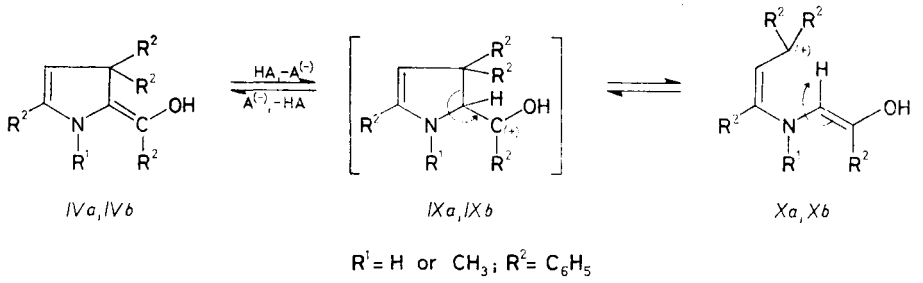
$$II + O_2 \rightleftarrows VII + O_2^{(\cdot-)} + Na^{(+)}$$



SCHEME 2

equilibrium according to which an aminyl radical *VII* was generated had obviously to preceed; this radical isomerizes to an energetically apparently more stable C-radical *VIII*. Recombination with the radical anion $O_2^{(\cdot)}$ followed by recyclization and hydrolysis, and possibly alkylation can lead to *IVa* and *IVb*, respectively. It is worth noting that contraction of the six-membered heterocycle to a five-membered one is topologically similar to oxidation of quaternary pyridinium salts in alkaline medium[6].

Compounds *IVa*, *IVb* possess properties of an acidobasic indicator in the presence of protic acids (cf. the UV spectra in Fig. 1). Formation of coloured cations is explained in Scheme 3. It assumes an extreme lability of products of a usual C-protona-



SCHEME 3

tion of enols *IVa* and *IVb* with a cyclic structure *IXa*, *IXb* undergoing cleavage of the heterocyclic ring under formation of delocalized cations *Xa*, *Xb*, close to vinylogues of triphenylmethane dyes. The proposed structures *Xa*, *Xb* are in accord with the ^{1}H NMR spectra of *IVa*, *IVb* measured in deuteriochloroform solutions; after acidification with trifluoroacetic acid a downfield shift of the olefinic proton in position 4 occured. The respective signals for compounds *IVa* and *IVb* after acidification

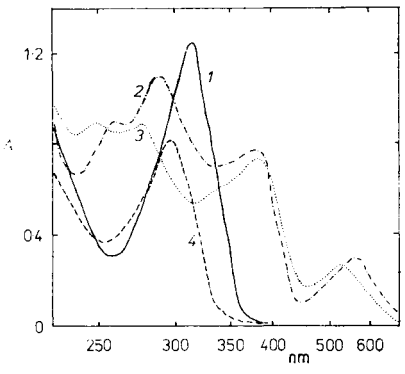


FIG. 1

Ultraviolet spectra of compounds *IVa* and *IVb* ($5 \cdot 10^{-5}$ M solution in ethanol). *1* Compound *IVa*; *2* compound *IVa* after acidification with H_2SO_4; *3* compound *IVb* after acidification with H_2SO_4; *4* compound *IVb*

lay at δ 6·69 and 6·61. Due to the delocalized positive charge effect a deshielding of proton signals of one aromatic ring in compounds *Xa*, *Xb* and a downfield shift of the N-methyl group in compound *Xb* took place. Reversibility of this reaction was confirmed by ^{1}H NMR spectra of *Xa* and *Xb* after neutralization with sodium hydroxide directly in the cuvette: the samples become colourless and the spectra were identical with those of the original compounds *IVa* and *IVb*.

EXPERIMENTAL

The temperature readings are uncorrected. The melting points were measured on a Boetius micro hot-stage. The IR spectra of chloroform and the UV spectra of ethanolic solutions were recorded with a Perkin–Elmer model 325, and Specord M-40 spectrophotometers, respectively. The mass spectra were taken with a Jeol DX 303/DA 5 000 (direct inlet system, 70 eV), and the NMR spectra with a Bruker AM 400 spectrometers, respectively. Experimental parameters: internal reference tetramethylsilane ($J = 0$ ppm), 400·134 MHz (65 K data points, digital resolution 0·184 Hz/point, pulse width 4 μs, temperature 297—350 K) for ^{1}H NMR and 100·61 MHz (65 K data points, digital resolution 0·9 Hz/point) for ^{13}C NMR; technique: APT; $CDCl_3$.

The starting dihydropyridine *I* was synthesized according to Peres de Carvalho[1,7]; crystallization from acetone gave a product melting at 232—234°C.

General Procedure for Preparation of Compounds *III*

Sodium hydride (0·1 g, 4·2 mmol) was added to a stirred suspension of compound *I* (0·5 g, 1·3 mmol) in dry dimethylformamide (5 ml). Stirring was continued at 40°C for 0·5 h, alkyl halogenide (5 mmol) in dimethylformamide (5 ml) was added at this temperature and the mixture was decomposed after 1 h by addition of water (10 ml). The precipitate was filtered off and washed with methanol.

If no solid separated (compounds *IIId*—*IIIf*, *IIIh*), the product was taken into benzene. The combined organic layers were washed with water to a neutral reaction, dried with sodium sulfate, the solvent was evaporated and the oily product crystallized under a layer of methanol (excepting *IIIf*). The product was purified by crystallization from acetone, or by chromatography on a silica gel column with benzene (compounds *IIIf* and *IIIh*). Data characterizing compounds *IIIa*—*IIIh* are listed in Tables I—III.

Alkylation with 2-propyl chloride followed by decomposition of the mixture, extraction with benzene and evaporation of the solvent afforded an oily product (0·5 g), which was chromatographed on a silica gel column with benzene. The first fraction (0·20 g of oil, 40%) was not succeeded to crystallize; its ^{1}H NMR spectrum indicated the content of 1-(2-propyl)-2,4,4,6-tetraphenyl-1,4-dihydropyridine (*IIIi*) to be only 5%. The second fraction yielded the starting *I* (0·30 g, 60%). Attempts to alkylate *I* with tert-butyl, trimethylsilyl, and cyclohexyl chlorides, 1,2-dibromomethane and ethyl bromacetate resulted in failure; work-up of the mixture afforded the starting material *I* only.

2-(1-Hydroxybenzylidene)-3,3,5-triphenyl-2,3-dihydropyrrole (*IVa*)

Sodium hydride (0·1 g, 4·2 mmol) was added to a stirred suspension of substance *I* (0·5 g, 1·3 mmol) in dry dimethylformamide (5 ml) and the mixture was kept at 40°C under exclusion of air humidity. Water (10 ml) was added and the product was extracted with benzene. The combined organic layers were washed with water to a neutral reaction, dried with sodium sulfate, benzene was

distilled off and the oily dark brown residue (0·5 g) was chromatographed on a silica gel column with benzene. A pure fraction containing *IVa* (0·35 g, 67%) as a white substance (R_F 0·4 on Silufol sheets, benzene) was crystallized from benzene; m.p. 208—211°C (decomp.). For $C_{29}H_{23}$. .NO (401·5) calculated: 86·75% C, 5·77% H, 3·49% N; found: 86·50% C, 5·84% H, 3·36% N. IR spectrum cm^{-1}: 3 580 (O–H); 3 458 (N–H); 3 060, 3 005 (Ar–H); 1 602, 1 580 (C=C). ^{1}H NMR spectrum: 8·39 s, 1 H (N–H, upfield shift at elevated temperature); 7·18—7·42 m, 20 H $(C–H)_{Ar}$; 6·01 d, 1 H (^4J(H, H) = 3 Hz, 4-CH); 2·91 s, 1 H (upfield shift at elevated temperature). ^{13}C NMR spectrum (for numbering cf. formula *IV*): 130·17 (C-2), 79·32 (C-3), 147·95 (C-3a), 127·56 (C-3*b*), 127·68 (C-3c), 123·60 (C-3d), 109·65 (C-4), 133·67 (C-5), 132·07 (C-5a), 128·85 (C-5b), 128·62 (C-5c), 127·37 (C-5d), 129·37 (C-6), 129·82 (C-6a), 128·40 (C-6b), 128·87 (C-6c), 126·36 (C-6d). UV spectrum, nm (log ε): 209 (3·55), 316 (3·34). Mass spectrum, *m/z* (relative intensity, %): 401 (50), 385 (7), 384 (19), 383 (30), 382 (5), 325 (7), 324 (22), 306 (7), 280 (4), 279 (6), 246 (4), 203 (4), 202 (4), 178 (12), 115 (4), 106 (7), 105 (100), 77 (21), 51 (3).

2-(1-Hydroxybenzylidene)-1-methyl-3,3,5-triphenyl-2,3-dihydropyrrole (*IVb*)

Sodium hydride (0·18 g, 7·5 mmol) was added to a stirred suspension of compound *I* (1 g, 2·6 mmol) in dry dimethylformamide (10 ml) at 40°C under exclusion of air humidity. Methyl iodide (1·42 g, 10 mmol) in dry dimethylformamide (5 ml) was added and the mixture was stirred at an ambient temperature for 3 h. Work-up of the mixture was analogous with that of *IVa*. The oil (1·1 g) chromatographed over a silica gel with benzene furnished two fractions. The first one (0·5 g, 45%) of photochromic *IIIa* gave on crystallization from acetone crystals of m.p. 181—182°C, the second one (0·6 g of oil) overlayed with light petroleum crystallized to give *IVb* (0·35 g, 38%), R_F 0·56 (Silufol sheets, benzene). After recrystallization from benzene the m.p. was 167—169°C. For $C_{30}H_{25}NO$ (415·5) calculated: 86·71% C, 6·06% H, 3·37% N; found: 86·65% C, 6·10% H, 3·29% N. IR spectrum, cm^{-1}: 3 560 (O–H); 3 060, 3 005 (Ar–H); 1 600 (C=C). ^{1}H NMR spectrum: 7·09—7·39 m, 20 H $(C–H)_{Ar}$; 5·75 s, 1 H (4-CH); 3·33 s, 3 H (CH_3); 2·65 s, 1 H (O–H, upfield shift at elevated temperature). ^{13}C NMR spectrum (for numbering cf. formula *IV*): 33·19 (C-1), 133·04 (C-2), 79·34 (C-3), 148·15 (C-3a), 127·48 (C-3b), 127·63 (C-3c), 126·66 (C-3d), 110·45 (C-4), 133·41 (C-5), 133·35 (C-5a), 128·28 (C-5b), 128·81 (C-5c), 128·00 (C-5d), 128·90 (C-6), 131·99 (C-6a), 128·33 (C-6b), 131·42 (C-6c), 126·76 (C-6d). UV spectrum, nm (log ε): 206 (3·62), 297 (3·15). Mass spectrum, *m/z* (relative intensity, %): 416 (4), 415 (13), 399 (5), 398 (7), 339 (8), 338 (30), 322 (4), 260 (4), 233 (4), 118 (5), 106 (8), 105 (100), 97 (5), 85 (4), 83 (4), 81 (4), 77 (20), 71 (6), 69 (8), 57 (11), 55 (6), 43 (8), 41 (4).

For measuring the NMR *spectra the authors wish to thank colleagues from the Laboratory of* NMR *spectroscopy (Head Dr P. Trška).*

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Translated by Z. Votický.