ON DIHYDROPYRIDINES. XXIV.*

PARTIAL HYDROGENATION OF SOME 3,5-DICYANOPYRIDINES

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After hydrogenation of 3,5-dicyanopyridine (*I*) and 3,5-dicyano-4-methylpyridine (*II*) on palladium a mixture of 1,2- and 1,4-dihydroisomers *V* and *IX*, and 1,2-dihydro derivative *X* were isolated from the reaction mixture. In the case of the hydrogenation of 3,5-dicyano-2,6-dimethylpyridine (*III*) and 3,5-dicyano-2,4,6-trimethylpyridine (*IV*) only traces of a mixture of isomeric dihydropyridines *VII*, *XI*, and *VIII*, *XII* were found. The mechanism of hydrogenation is discussed from the point of view of bicentric localisation energies, within the frame of the simple HMO theory.

The possibility of the formation of dihydro derivatives by hydrogenation of pyridine compounds is interesting from the point of view of the mechanism of this reaction and also, in certain cases, from the preparative point of view. While great attention has been devoted to the study of the formation of dihydropyridines after an attack of the pyridine nucleus by nucleophilic agents, hydrogenation is still limited to a small number of examples[1-5]. The papers mentioned show that dihydro intermediates may be found mainly in cases when 3,5-disubstituted pyridine derivatives serve as the starting material. In this paper our aim was to investigate the hydrogenation of 3,5-dicyanopyridines *I*–*IV* under mild conditions (atmospheric pressure, room temperature, palladium catalyst).

Substance *I* was hydrogenated[1] in acetic acid on platinum. The authors did not isolate any product, but they supposed the presence of 1,4-dihydropyridine derivative *V* in the reaction solution on the basis of its ultraviolet spectrum. The isolation of 1,2-dihydro derivative *X* and of the analogous 4-ethyl homologue was successful[2] after the hydrogenation of corresponding 2,6-dichloro-3,5-dicyano-4-alkylpyridines *XIII* on palladium. In contrast to this, an analogous hydrogenation of 3,5-dicyano-2,4,6-trimethylpyridine (*IV*) was unsuccessful, due evidently to steric reasons[5].

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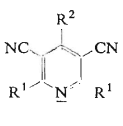
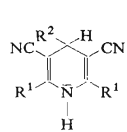
All attempts at the hydrogenation of substances *I–IV* were carried out under standard conditions in ethanolic solutions, using palladium on barium carbonate or sulfate as the catalyst. From the course of the hydrogenation curves represented on Fig. 1 it is evident that the rate of hydrogenation of the investigated 3,5-dicyano derivatives decreases in the following sequence: $I > II > III > IV$, *i.e.* with an increasing number of methyl groups on the heteroaromatic nucleus. In the case of substances *III* and *IV* it was impossible to attain a larger consumption of hydrogen than 0·9 mol, even after prolonged hydrogenation procedure. In all experiments we were able to demonstrate in the reaction mixture by chromatography combined with spectrophotometry (for the procedure *cf.* ref.[6,7]) some of 1,2- and 1,4-dihydropyridine derivatives *V–XII*, but regularly accompanied by other reaction products of an unknown structure. From Table I it is evident that the preparatively determined yields of dihydro derivatives are not high and that they depend on the hydrogen consumption and on the palladium carrier.



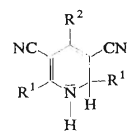
I–IV, XIII

I, V, IX, $R^1 = R^2 = H$
II, VI, X, $R^1 = H$, $R^2 = CH_3$
III, VII, XI, $R^1 = CH_3$, $R^2 = H$,



V–VIII

IV, VIII, XII, $R^1 = R^2 = CH_3$
XIII, $R^1 = Cl$, $R^2 = CH_3$ or C_2H_5



IX–XII

Hydrogenation of 3,5-dicyanopyridine (*I*) led to a mixture of 3,5-dicyano-1,2-dihydropyridine (*IX*) and 3,5-dicyano-1,4-dihydropyridine (*V*) in which the former distinctly prevailed. In addition to this two, other unidentified compounds are formed which may be the products of a subsequent hydrogenation or disproportionation of dihydro derivatives *V* and *IX*; this follows from the independent hydrogenation of a mixture of substances *V* and *IX*, during which the mentioned substances are

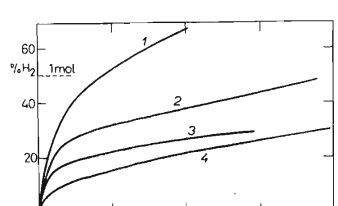


FIG. 1

Hydrogenation Curves of Substances *I – IV* (25°C, 750 Torr, $Pd/BaCO_3$)
1 3,5-Dicyanopyridine (*I*); *2* 3,5-dicyano-4-methylpyridine (*II*); *3* 3,5-dicyano-2,6-dimethylpyridine (*III*); *4* 3,5-dicyano-2,4,6-trimethylpyridine (*IV*).

formed. From the occurrence of the maxima of stretching vibrations of the conjugated cyano groups (2238 cm^{-1}) and N—H bonds (~3 400 cm^{-1}) in their infrared spectra it can be supposed that they are tetrahydro derivatives (see analogous results in[4,5,8]).

3,5-Dicyano-4-methylpyridine (*II*) gives 3,5-dicyano-4-methyl-1,2-dihydropyridine (*X*) as the main product, accompanied by less than 2% of 3,5-dicyano-4-methyl-1,4-dihydropyridine (*VI*) when palladium on barium carbonate was employed. The formation of substance *X* after hydrogenation of 2,6-dichloro derivative *XIII*[2] may be explained by the scheme $XIII \xrightarrow{H_2} II \xrightarrow{H_2} X$. In addition to this, similarly as in the case of the hydrogenation of compound *I*, a mixture of two additional compounds is formed which have the character of tetrahydro derivatives (stretching vibration of the conjugated C≡N groups at 2200 and 2233 cm^{-1}, and N—H bonds about 3460 cm^{-1}), which were found identical with the product of hydrogenation of pure 1,2-dihydro derivative *X* on palladium and barium sulfate.

The hydrogenation of 3,5-dicyano-2,6-dimethylpyridine (*III*) and 3,5-dicyano-2,4,6-trimethylpyridine (*IV*) takes place very slowly, in agreement with the findings of Eisner[5]; in the reaction mixture the starting substances *III*, *IV* (67—74%) prevail, but five to six other substances are also present. Among them it was possible to show in the first case the presence of 3,5-dicyano-2,6-dimethyl-1,2-dihydropyridine (*XI*) and 3,5-dicyano-2,6-dimethyl-1,4-dihydropyridine (*VII*), and in the second case the presence of analogous 2,4,6-trimethyl homologues *XII* and *VIII*. This was possible due to their characteristic behaviour in ultraviolet light (see for example [7]). Unfortunately, the content of dihydropyridines *VII*, *VIII*, *XI*, and *XII* was low, and it was impossible to carry out a spectrophotometric analysis of the relative representation of single isomers after their separation. An approximate estimate from the comparison of the size of their spots on chromatograms with standards shows that 1,2-dihydro isomers *XI* and *XII* prevail to a certain extent. Other unidentified substances had the character of tetrahydro derivatives (absorption maxima at 3010—3013 cm^{-1}, 2227—2230 cm^{-1}), and carbonyl compounds (1685—1688 cm^{-1} and 1738—1730 cm^{-1}).

The above results show that the hydrogenation of compounds *I*—*IV* gives rise to identical dihydro derivatives, similarly to the reaction with complex hydrides[9,10], but the yields are much lower. In the case of substance *I*, and probably also *III* and *IV*, the ratio of 1,2- and 1,4-isomers is quite different; in contrast to nucleophilic reactions[7,9,10] the 1,2-dihydro derivative distinctly prevails. This fact cannot be explained within the frame of the simple HMO theory by means of monocentric indices of chemical reactivity which characterise the homolytic reactivity by free valences, atomic localization energies, and superdelocalizabilities (compare these data for substances *I*—*IV* with those in communications [11—13]). The corresponding idea that in the first step of hydrogenation an attack on the most sensitive place of the molecule should occur, under formation of a sigma complex, and that in the subsequent step the addition of another hydrogen atom takes place, does not cor-

respond to our experimental results. Therefore, we decided to apply bicentric localization energies L_{ij} in which it is supposed that in the structurally close activated complex of hydrogenation two atomic centers i and j will be eliminated from the conjugation simultaneously[14,15]. This means that before the desorption of the products a simultaneous attack on two positions of the heterocyclic nucleus by hydrogen atoms should take place. This mechanism of hydrogenation of 3,5-disubstituted derivatives of pyridine is also supported by some experimental results of Lyle and Mal'ett[4]. In Table II some values for L_{ij} for a radical attack are given which were calculated by the simple HMO method[16]. It is evident that the lowest values of this index correspond in accordance with expectations to 1,2- and 1,4-additions to the heteroaromatic nucleus, while

TABLE I

Review of Hydrogenations of 3,5-Dicyanopyridines *I*–*IV* to Corresponding Dihydropyridines

Compound	Consumption mol. H_2	Time h	Catalyst	Dihydropyridines formed	Yield[a] %
I	0·8	1·25	$Pd/BaSO_4$	*V*, *IX*	7·5
I	1·0	2·35	$Pd/BaSO_4$	*V*, *IX*	2·2
I	1·3	1·20	$Pd/BaCO_3$	*V*, *IX*	17·5[b]
I	2·5	7·5	$Pd/BaCO_3$	*V*, *IX*	34·5[c]
II	1·0	6	$Pd/BaSO_4$	*X*	28·0
II	1·3	6	$Pd/BaCO_3$	*VI*[d], *X*	27·4
III	0·8[e]	15	$Pd/BaSO_4$	*VII*, *XI*	4·1
III	0·6[e]	15	$Pd/BaCO_3$	*VII*, *XI*	[d]
IV	0·9[e]	17	$Pd/BaSO_4$	*VIII*, *XII*	2·3
IV	0·6[e]	17	$Pd/BaCO_3$	*VIII*, *XII*	[d]

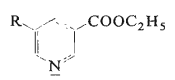
[a] Determined by preparative column chromatography; [b] of this 86% of substance *IX*; [c] of this 83% of substance *IX*; [d] content lower than 2%; [e] final consumption.

TABLE II

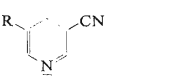
Bicentric Radical Localization Energies of Substances *I*–*IV*. Empirical Parameters[11,24]: $h_N = 0{\cdot}5$; $K_{CN} = 1{\cdot}0$ (heterocyclic ring); $h_N = 0{\cdot}7$; $k_{CN} = 1{\cdot}4$ (CN groups); $h_{CH_3} = 2{\cdot}0$; $k_{C-CH_3} = 0{\cdot}7$.

Substance	Attacked positions *i*	*j*	type	$L_{ij}(\beta)$	Substance	Attacked positions *i*	*j*	type	$L_{ij}(\beta)$
I	1	2	*ortho*	3·507	*II*	1	2	*ortho*	3·511
I	1	3	*meta*	5·611	*II*	1	4	*para*	4·150
I	2	3	*ortho*	3·868	*III*	1	2	*ortho*	3·656
I	3	4	*ortho*	3·825	*III*	1	4	*para*	3·950
I	2	5	*ortho*	4·319	*IV*	1	2	*ortho*	3·659
I	1	4	*para*	3·972	*IV*	1	4	*para*	4·128

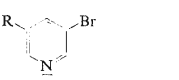
it applies that $L_{12} < L_{14}$. If the fact that the 1,2-addition in substances *I*–*IV* is twice as probable from the statistical point of view, is taken into account it seems that our experimental results agree well with the given localization energies. A more accurate measurement of the reactivity of compounds *I*–*IV* is hindered by the above mentioned subsequent and probably also disproportionation reactions[5,8,17]; hence, only the results of the hydrogenation of pyridine derivatives *I* and *II* may be interpreted reliably, as the products may contain dihydropyridines *V*, *IX*, and *X* as the prevailing products (Table I). When the rate of hydrogen consumption in the initial stage of hydrogenation of substances *I* and *II* is compared (Fig. 1), it is evident that the reactivity of derivative *I* is higher, which is in good accordance with the lower value of $L_{12} = 3{\cdot}507\beta$, than that of compound *II*, which has $L_{12} = 3{\cdot}511\beta$ (Table II).



XIV, R = $COOC_2H_5$
XV, R = $CONH_2$
XVI, R = CN



XVII, R = H
XVIII, R = Br
XIX, R = $CONH_2$



XX, R = $CONH_2$
XXI, R = $COOC_2H_5$
XXII, R = Br

In order to obtain 3,5-dicyanopyridine (*I*) some remaining possibilities were tested, in addition to earlier procedures[1,7,19]. It was found that diethyl ester of dinicotinic acid (*XIV*) under the effect of ethanolic ammonia gives monoamide *XV* in high yield. From it ethyl 5-cyanonicotinate (*XVI*) may be prepared easily by dehydration[18]. Compound *XVI* was converted by a known procedure[7] to substance *I via* amide *XIX*. In the case of the second route 3-cyanopyridine (*XVII*) was brominated to give a mixture of 3-bromo-5-cyanopyridine (*XVIII*) and 5-bromonicotinamide (*XX*). Amide *XX* which was also prepared from the corresponding ester *XXI* again gave on dehydration with phosphorus oxychloride nitrile *XVIII* which under the effect of copper cyanide at elevated temperature gave in dimethylformamide dinitrile *I*. The latter compound, *I*, was obtained eventually in 23 % yield also by an analogous reaction from 3,5-dibromopyridine (*XXII*).

EXPERIMENTAL

Temperature data are uncorrected. Unless stated otherwise the melting points were determined on a Kofler block. The infrared spectra were measured on a Zeiss (Jena) model UR 10 spectrophotometer, the ultraviolet spectra on a CF 4 NI (Optica, Milano) apparatus and the PMR spectra on a spectrometer Tesla BS 477 (60 MHz, internal standard hexamethyldisiloxane, 9·948τ). Chromatography was carried out on neutral alumina, activity II (Brockmann), detection in thin-layer chromatography by exposure to iodine vapours and UV light.

Hydrogenation of 3,5-Dicyano Derivative *I*–*IV*

A solution of the investigated substance (100 mg) in ethanol (20 ml) was hydrogenated in the presence of corresponding palladium catalyst at 25 ± 1°C, at atmospheric pressure and at a constant rate of an electromagnetic stirrer. The reaction was interrupted either after the absorption of the chosen consumption of hydrogen, or allowed to proceed until the clearly observable consumption stopped (Table I). The catalyst was then filtered off and washed with ethanol. The filtrate was evaporated under exclusion of air *in vacuo* at a temperature not exceeding 25°C, and the residue was dissolved in a suitable solvent and chromatographed on a column of alumina.

The composition of single fractions was followed by means of thin-layer chromatography on the same adsorbent. Fractions containing dihydropyridine derivatives were combined, evaporated, and submitted to spectrophotometric analysis if necessary[6]. The yields given in Table I were obtained by weighing of dihydropyridines obtained in this manner.

Hydrogenation of substance *I* (50 mg in 100 mg of $Pd/BaCO_3$) (ref.[20]) was allowed to proceed until 2·5 molar equivalents of hydrogen were absorbed. Working up and chromatography on 25 g of alumina (chloroform) gave 17·5 mg of a mixture of dihydro derivatives *V* and *IX* (R_F 0·21 and 0·23 resp., in chloroform) in addition to 20 mg of a mixture of two additional substances (R_F 0·48 and 0·36) identical with the products of hydrogenation of dihydropyridines *V* and *IX*. In analogy to this after hydrogenation of 200 mg of substance *I* on 400 mg of $Pd/BaSO_4$ (ref.[20]), and the consumption of 0·8 molar amount of hydrogen, 121 mg of the unreacted starting compound *I* were isolated by sublimation at 80–90°C/10 Torr. Further, 15 mg of a mixture of dihydro derivatives *V* and *IX* and 54 mg of a non-crystalline fraction containing substances of R_F 0·36 and 0·48. IR spectra (in chloroform): 792, 813, 898, 1115, 1242, 1268, 1430, 1462, 1503, 1578, 1643, 2202, 2239, 2852, 2930, 3010, 3028, 3390 (a diffuse band), 3468 cm^{-1}.

400 mg of 4-methyl derivative *II* (ref.[2], m.p. 84–85°C) were hydrogenated on 800 mg of $Pd/BaSO_4$ until one mol of hydrogen was absorbed. The residue after the evaporation of the solvents and dissolution in chloroform was chromatographed on 40 g of alumina, to give 213 mg of the starting compound *II* (R_F 0·80; chloroform with 2% of ethanol), 114 mg of 1,2-dihydro derivative *X* (R_F 0·19), m.p. 218–219°C (lit.[9,10] m.p. 214–223°C), and 19 mg of a mixture of two substances (R_F 0·27 and 0·37) identical with the products of hydrogenation of dihydropyridine *X*. IR spectrum (in chloroform): 825, 1100, 1240, 1263, 1421, 1470, 1522, 1586, 1638, 1692 (inflexion), 1726, 2200, 2233, 2870 (inflexion), 2928, 2963, and 3460 cm^{-1}. In another experiment 200 mg of *II* were hydrogenated on 400 mg of $Pd/BaCO_3$ (ref.[20]) with 1·3 mol of hydrogen. Employing an analogous procedure as in the preceding case 56 mg of dihydro derivative *X*, m.p. 222–223°C, were isolated from the reaction mixture. According to thin-layer chromatography it contained traces of 1,4-dihydro isomer *VI*.

Hydrogenation of 200 mg of 2,6-dimethyl derivative *III* (ref.[21]) was carried out in double dilution (because of its limited solubility), and the products were investigated after the consumption of hydrogen ceased (Table I). When 400 mg of $Pd/BaSO_4$ were used, chromatography on 50 g of alumina with benzene and then chloroform gave 153 mg of the starting compound *III*, m.p. 129–130°C (R_F 0·69; chloroform and 1% ethanol), 4 mg of a mixture of 1,2- and 1,4-dihydro derivatives *VII* and *XI* (R_F 0·15 and 0·16), and 3 mg of two unidentified compounds (R_F 0·29 and 0·56). In an analogous manner hydrogenation of 400 mg of 2,4,6-trimethyl derivative *IV* (ref.[21]) gave 283 mg of the starting compound *IV* (R_F 0·74; chloroform), 9 mg of a mixture of 1,2- and 1,4-dihydro derivative *VIII* and *XII* (R_F 0·29 and 0·30), and 4 mg of an unidentified substance of R_F 0·43.

Hydrogenation of 3,5-Dicyanodihydropyridine *V*, *IX*, and *X*

A mixture of dihydro derivatives *V* and *IX* (13 mg) isolated after hydrogenation of substance *I* was hydrogenated in 20 ml of ethanol on 100 mg of Pd/C (ref.[22]). After 16 hours the consumption of hydrogen was approximately one molar (approx. 2 ml), and the originally yellow solution was decolorized. According to thin-layer chromatography the reaction mixture contained the initial 1,4-dihydro derivative *V*, and both substances of R_F 0·36 and 0·48 (chloroform) present in the reaction mixture after hydrogenation of pyridine derivative *I*. Analogously, 40 mg of 1,2-dihydro derivative *X* were hydrogenated on 160 mg of $Pd/BaSO_4$. After three hours one molar equivalent of hydrogen (approx. 6·5 ml) was absorbed. The reaction mixture did not contain any starting dihydropyridine *X*, but the presence of two substances of R_F 0·27 and 0·37 (chloroform and 2%

of ethanol) identical with the products of hydrogenation of substance *II*. When $Pd/BaSO_4$ was used in the presence of substances *V*, *IX*, and *X*, there was no consumption of hydrogen even after 5 hours saturation.

5-Ethoxycarbonylnicotinamide (*XV*)

A solution of 6 g of diethyl ester *XIV* (ref.[19]) in 50 ml of ethanol saturated with gaseous ammonia at room temperature was allowed to stand for one week. The separated crystals were filtered off under suction and crystallised from dimethylformamide. Yield of amide *XV*: 4·39 g (84%); m.p. 198°C (lit.[18] gives m.p. 193·5°C). For $C_9H_{10}N_2O_3$ (194·2) calculated: 55·66% C, 5·19% H, 14·43% N; found: 55·78% C, 5·33% H, 14·53% N.

5-Bromonicotinamide (*XX*)

A suspension of 40 g of ethyl 5-bromonicotinate (*XXI*) (ref.[7]) in 400 ml of aqueous 25% ammonia was stirred and mildly refluxed for 5 hours. After cooling the reaction product was filtered off, washed with ice-cold water, and dried. Yield 22·1 g (63%) of substance *XX*, m.p. 222—223°C. For $C_6H_5BrN_2O$ (201·0) calculated: 35·85% C, 2·51% H, 39·75% Br, 13·94% N; found: 36·19% C, 2·68% H, 40·21% Br, 13·84% N.

5-Bromo-3-cyanopyridine (*XVIII*)

A) To a suspension of 20 g of amide *XX* in 45 ml of pyridine 20 ml of phosphorus oxychloride were added dropwise under cooling. The mixture was stirred for 1 hour at room temperature, and then 4 hours at 50°C. After evaporation by distillation of excess reagent, the residue was decomposed with ice and water and neutralised to pH 9 with dilute ammonia. The mixture was then extracted continually with chloroform, the extract was dried over magnesium sulfate, and evaporated *in vacuo* at 20°C. The residue was sublimated at 60—70°C/3 Torr, yielding 7 g (38%) of nitrile *XVIII*, m.p. 102—103°C. Repeated sublimation gave a preparation of m.p. 103—104°C. PMR spectrum (in deuteriochloroform) gives a spin ABX system with an AB component of two α protons at $\sim$0·9τ (quartet), and an X component of one γ proton at $\sim$1·4τ (triplet). For $C_6H_3BrN_2$ (183·0) calculated: 39·38% C, 1·65% H, 43·67% Br, 15·30% N; found: 39·69% C, 1·64% H, 43·69% Br, 15·21% N.

B) To a solution of 10 g of 3-cyanopyridine (*XVII*) (ref.[22]) in 24 ml of thionyl chloride 12 ml of bromine were added dropwise under cooling and the mixture was refluxed for 40 hours. The volatile material was distilled off *in vacuo* (water bath) and the residue was diluted with water and alkalised with potassium carbonate. The separated crystals (0·85 g) were filtered off with suction and crystallised from water. M.p., 221—222°C, shows that it is amide *XX*. The remaining solution was submitted to continuous extraction with chloroform and the extract was dried over magnesium sulfate and evaporated at 20°C *in vacuo*. Yield 8·5 g (48%) of substance *XVIII*, m.p. 102—103°C (after sublimation at 80°C/13 Torr).

3,5-Dicyanopyridine (*I*)

A) 8 g of 5-bromo derivative *XVIII*, 5·25 g of copper(I)cyanide and 30 ml of dimethylformamide were refluxed for 3·5 hours. The solvent was evaporated under reduced pressure (13 Torr), while the temperature increased steadily to 130°C. The last fractions of the distillate were collected separately and they gave a small amount of substance *I* after dilution with water. The bulk of the product was obtained by distillation of the residue, in the fraction boiling between 240

and 280°C/13 Torr. This material was crystallised from ethanol and sublimated at 90°C/13 Torr. Total yield 3 g (36%) of dicyano derivative *I*, m.p. 111–113°C. Lit.[1,7] gives m.p. 113–113·5°C.

B) 31·5 g of 3,5-dibromopyridine (*XXII*) (ref.[23]) and 80 ml of dimethylformamide were stirred with 26 g of copper(I)cyanide at 170°C for 3 hours. After cooling the reaction mixture was submitted to vacuum distillation in order to eliminate the main part of the solvent (from a water bath). Subsequent fractions were distilled off by increasing the temperature of the bath up to 220°C/13 Torr. Single fractions were diluted with equal amounts of water and the separated product, if any, was filtered off under suction. The solid residue was submitted eventually to thermal decomposition in vacuum (12 Torr), during which the main fraction of product *I* distilled over. The crude cyano derivative *I* was recrystallised from dilute ethanol and then sublimated at 80°C/8 Torr. Total yield was 3·85 g (23%) of substance *I*, m.p. 112°C.

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