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INVESTIGATION OF THE DIMERIZATION REACTION OF CERTAIN β-SUBSTITUTED PYRIDINE BASES IN THE PRESENCE OF METALLIC SODIUM AND RANEY Ni CATALYSTS

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UDC 542.97:547.82

Dipyridyls (Dipy) are mainly synthesized by dimerization of pyridine (Py) bases in the presence of metal catalysts [1-4]. The dimerization reaction of Py in the presence of alkali metals (Li, Na, K) and Raney Ni were previously studied by us in detail in [5, 6]. Based on an investigation of the kinetics of the process and analysis of the resulting intermediate and final products by spectroscopic methods, the mechanism of formation of Dipy in these reactions was studied in [7]. With the aim of obtaining new substituted Dipy derivatives and also of clarifying the influence of substituents in the Py nucleus on the dimerization reaction we have studied the dimerization of certain β-substituted Py bases, viz. β-picoline (3-methylpyridine), nicotinic acid methyl ester (3-carbomethoxypyridine), cordiamin (nicotinic acid diethylamide), anabasine [3-(piperid-2-yl)pyridine], and N-methylanabasine [3-(1-methylpiperid-2-yl)pyridine], in the presence of dispersed metallic sodium and Raney Ni.

It was shown that the nature and position of the substituent in the heterocycle showed an influence on the rate and direction of dimerization of Py derivatives and also on the yields of the final products. This is explained by two factors, by the actual change in π-electron density at the various positions of the Py ring in relation to the electron-donating and electron-accepting properties of the substituent and by the steric effect of the substituent.

It was shown using the example of the dimerization of β-picoline [8] in the presence of metallic sodium that the reaction proceeded under more forcing conditions compared with pyridine [4] and the yield of product grew with increasing reaction time (Table 1).

The steric factor of the substituent also had some influence on the rate of dimerization. Thus, dimerization of nicotinic acid methyl ester [9] and of cordiamin as opposed to Py and β-picoline was effected at a higher temperature and only in the presence of solvents (benzene, toluene, xylene, nitrobenzene) (see scheme at top of following page). Yields of dimers were somewhat lower than in the case of Py and β-picoline (see Table 1). This is seemingly explained by the fact that the basicities of nicotinic acid methyl ester and cordiamin at 4.9 and 3.6 respectively are significantly less than those of Py and β-picoline. Furthermore the more bulky substituents (CO_2Me and

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V. I. Lenin Tashkent State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2607-2611, November, 1983. Original article submitted March 28, 1983.

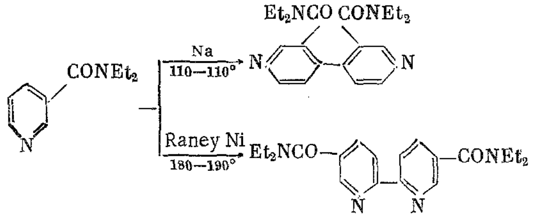
0568-5230/83/3211-2344$07.50

TABLE 1. Dimerization of Some β-Substituted Py Derivatives in the Presence of Na and Raney Ni Catalysts (ratio of initial reactants was 4:1 (molar) in an atmosphere of N_2)

Base	Condensing reagent	pKa of heterocycle	Solvent	T., °C	Time, h	Yield of dipyridyls, %		
						4,4′-	2,2′-	2,4′-
β-Picoline	Na	5,68	Excess of picoline	–5–0	48	Traces	–	–
The same	Na	5,68	The same	50–60	48	40	–	–
»	Na	5,68	»	110–115	24	10	30	–
Nicotinic acid methyl ester	Na	4,9	Benzene	80	30	60	–	–
Cordiamin	Na	3,6	Toluene	100–110	16	26,5	–	–
»	Raney Ni	3,6	Without solvent	180–190	10	–	93,2	–
Anabasine	Na	4,81	Benzene	50–60	30	55	–	8
N-Methylanabasine	Na	5,42	»	50–60	32	40	1	–
The same	Na	5,42	Xylene	120–130	30	30	20	–
»	Raney Ni	5,42	Without solvent	200–220	11	12	–	–

TABLE 2. Change of π-Electron Density of Some β-Substituted Py Derivatives

Base	$\Delta q\pi$		
	C^4	C^2	C^3
β-Picoline	0,017	0,1	–
Nicotinic acid methyl ester	0,01	0,002	0,004
Cordiamin	0,01	0,002	0,005
Anabasine	0,002	0,0009	0,002
N-Methylanabasine	0,015	–	0,004



CONEt_2) showed a greater influence on the conditions and direction of the dimerization. Anabasine and N-methyllanabasine were interesting subjects for dimerization investigations. With those subjects it was possible to show the influence of steric factors on the dimerization process since these bases are close to β-picoline and nicotinic acid methyl ester in basicity value of the pyridine ring. Consequently, they must not differ by much in their behavior in the studied reaction. Reaction of these compounds proceeded under conditions similar to those of the reaction of β-picoline and the corresponding 4,4′-Dipy derivatives were formed as the main reaction products [10, 11].

The special feature of the dimerization reaction of anabasine and N-methylanabasine under the action of metallic sodium was that in some cases the formation was observed of the corresponding 2,2′- and 2,4′-Dipy derivatives in higher yield in comparison with Py (see Table 1) [12, 13]. These data may probably be explained by the fact that the substituents (piperidyl and N-methylpiperidyl) may create definite steric difficulties for the entry of the second substituent into the neighboring position.

The obtained experimental data make it possible to draw the conclusion that the N atom of the Py heterocycle is the main para orienter in the dimerization reaction of β-substituted Py derivatives. The influence of this factor on the conduct of dimerization in the presence of Raney Ni is especially important. As opposed to Py dimerization was effected at 200-220°C with a reduction in the yield of the corresponding 2,2′-Dipy derivatives from 30 to 10-12% [14] (see Table 1).

The influence of the electronic structure of substituted Py on the dimerization process was clarified by analysis of the PMR spectra of these bases (Table 2).

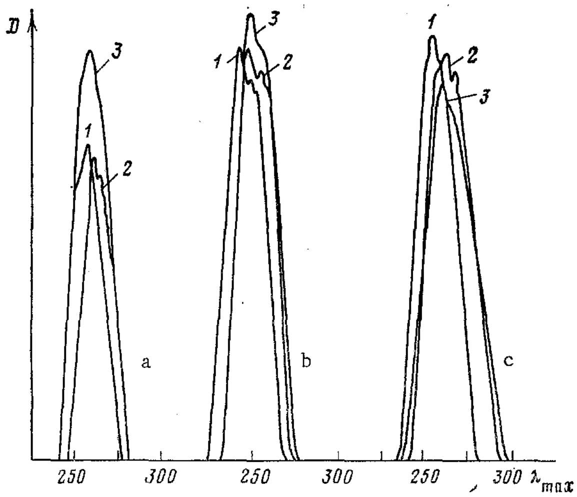


Fig. 1

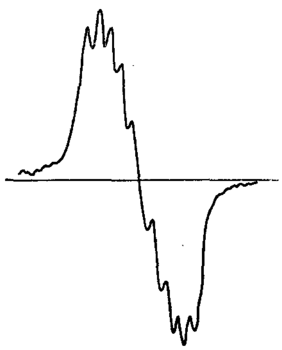


Fig. 2

Fig. 1. UV spectra, a: 1) β-picoline; 2) β-picoline + Na (after mixing); 3) β-picoline + Na (after 24 h); b: 1) anabasine; 2) anabasine + Na (after mixing); 3) anabasine + Na (after 24 h); c: 1) N-methylanabasine; 2) N-methylanabasine + Na (after mixing); 3) N-methylanabasine + Na (after 24 h).

Fig. 2. ESR spectrum of the σ complex formed on interacting β-picoline with metallic Na.

The greatest changes in π-electron density (see Table 2) were observed on the γ carbon atom at which dimerization was mainly effected. Study of the kinetics of dimerization of β-substituted Py-bases under the action of Na and Raney Ni by UV, IR, and ESR spectroscopic methods made it possible to characterize in more detail certain stages of the process and to propose a scheme for the mechanism of the dimerization reaction. It was shown by UV spectroscopy that transfer of an electron from metal to heterocycle was observed in the first stage of the reaction. Spectra were taken at the time of mixing and after 24 h in the 200-300 nm region characteristic of π-π* transitions in the aromatic systems.

Analysis of the UV spectra (Fig. 1) of β-picoline, anabasine, and N-methylanabasine showed that in the 250-280 nm region a shift was observed for the absorption maxima into the visible region at the time of mixing the reacting substances. The size of the displacement depended on the nature and position of the substituent in the Py ring. The observed displacements in the UV spectrum made a basis for suggesting that the initial stage of the dimerization reaction was the partial transfer of an electron from metal to heterocycle with the formation of a charge transfer complex (CTC). The following step of the process was complete transfer of an electron and the formation of an anion radical of the initial heterocycle which then attacked a neutral molecule and formed a paramagnetic σ complex. This was confirmed by the ESR spectrum (Fig. 2) as in the case of Py [7, 15].

The data obtained by us on studying the kinetics of formation of anion radicals and therefore of σ complexes of substituted Py made it possible to clarify certain of their differences in rate of formation in relation to the various factors and to the structure of the initial bases. Using the dimerization of β-picoline and N-methylanabasine with metallic Na as examples it was shown that the rate of formation of anion radicals of these bases and also their concentration in the reaction process depended little on time in difference to Py (Fig. 3).

The main factor contributing to the increase in rate of formation and accumulation of anion radicals of substituted Py was temperature (Fig. 4).

EXPERIMENTAL

PMR spectra were taken on a Varian XL-100 spectrometer in CCl_4, standard was TMS. IR spectra were recorded on a UR-20 spectrometer in KBr disks. UV spectra were taken on a Beckman-25 instrument in THF, concentration $2 \cdot 10^{-4}$ mole/liter. ESR spectra were drawn on a Varian E-4 radiospectrometer under conditions of slow running.

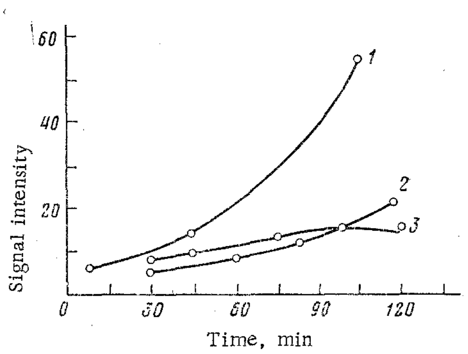


Fig. 3

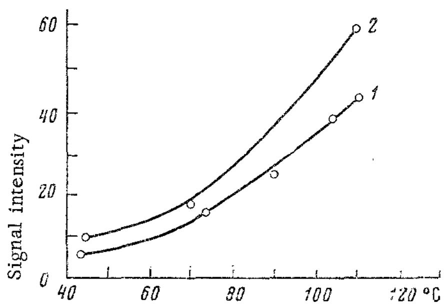


Fig. 4

Fig. 3. Change in intensity of ESR signal of σ complexes as a function of time: 1) pyridine; 2) β-picoline; 3) N-methylanabasine.

Fig. 4. Change of ESR signal intensity of σ complexes as a function of temperature: 1) β-picoline; 2) N-methylanabasine.

3,3'-Di-(N,N-diethylcarbamido)-4,4'-dipyridyl. Dispersed metallic sodium (2 g, 0.09 mole) was added gradually to a solution of cordiamin (64 g, 0.36 mole) in abs. toluene (50 ml) and the mixture stirred for 16 h at 100-110°C in a stream of N_2. After the end of the reaction the mixture was oxidized with O_2, the solvent distilled off, and the residue decomposed with water. The excess of cordiamin was extracted with petroleum ether. The residue (9.5 g), after removal of water, was chromatographed on SiO_2 (240 g). Elution with an acetone–water (15:2) mixture gave product (2.5 g, 26.5%), mp 136-137°C. IR spectrum (ν, cm^{-1}): 760, 790, 860, 890, 1030, 1100, 1520, 1620, 2850, 2920. PMR spectrum (100 MHz, δ, ppm): 1.13 t (12 H, CH_3), 3.33 q (8 H, CH_2), 7.08 dd (4 H, α-H), 8.50 dd (2 H, β-H). Found: C 67.50; H 7.39; N 15.23%. $C_{20}H_{26}N_4O_2$. Calculated: C 67.79; H 7.34; N 15.82%.

5,5'-Di-(N,N-diethylcarbamido)-2,2'-dipyridyl. A mixture of cordiamin (71.2 g, 0.4 mole) and activated Raney Ni (5.9 g, 0.1 mole) was stirred for 10 h at 180-190°C in a stream of N_2. The excess of cordiamin was extracted with petroleum ether. The residue (2.5 g) was chromatographed on SiO_2 (70 g). Elution with an acetone–water (25:2) mixture gave product (2.33 g, 93.2%), mp 132-133°C. IR spectrum (ν, cm^{-1}): 760, 860, 1100, 1120, 1570-1700, 2980. PMR spectrum (100 MHz, δ, ppm): 1.13 t (12 H, CH_3), 3.33 q (8 H, CH_2), 7.4 m (2 H, γ-H), 7.8 m (2 H, α-H), 8.6 m (2 H, β-H). Found: C 67.84; H 7.23; N 15.39%. $C_{20}H_{26}N_4O_2$. Calculated: C 67.79; H 7.34; N 15.82%.

CONCLUSIONS

1. The dimerization of β-substituted pyridine bases depends effectively on the steric factors of the substituents in the pyridine ring.

2. The formation of the corresponding dimers from pyridine bases passes through a charge transfer complex in the first stage of the reaction with subsequent formation of anion radicals and paramagnetic σ complexes.

3. On interacting cordiamin with metallic sodium and Raney Ni new β-substituted derivatives of 4,4'- and 2,2'-dipyridyls were obtained, viz. 3,3'-di-(N,N-diethylcarbamido)-4,4'-dipyridyl and 5,5'-di-(N,N-diethylcarbamido)-2,2'-dipyridyl.

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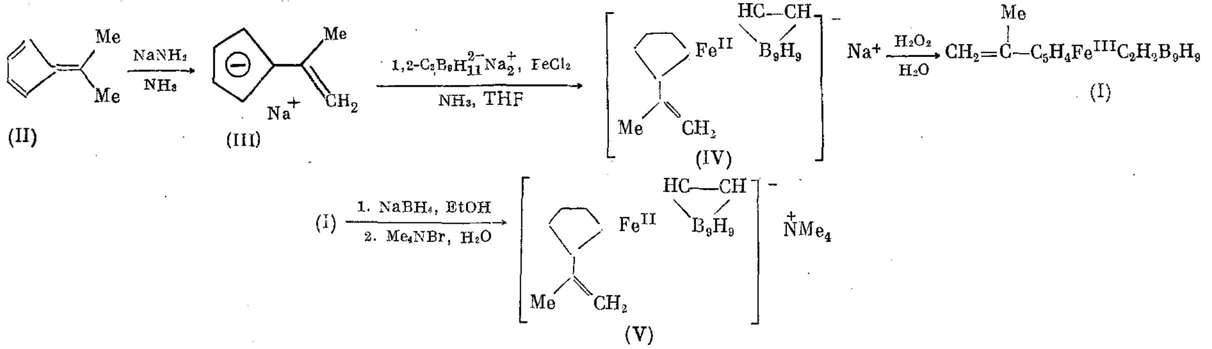
SYNTHESIS OF η^5-ISOPROPENYLCYCLOPENTADIENYL-η^5-(3)-1,2-DICARBOLLYLIRON(III) AND THE PREPARATION OF ITS CARBOCATION STABILIZED WITH A η^5-1,2-$C_2B_9\bar{H}_{11}$-3-Fe^{II}-η^5-C_5H_4 GROUP

L. I. Zakharkin and V. V. Kobak

UDC 542.91:541.49:547.1'13:547.1'127

The ability of the ferrocenyl group to stabilize the carbocationic center connected with it has been studied widely [1]. The ability of the η^5-C_5H_5-3-Fe^{II}-η^5-1,2-$C_2B_9\bar{H}_{10}$-1- group to stabilize a carbocationic center linked with the C atom of the η^5-carborane ligand was also shown by us previously in [2-5]. In this connection, it was of interest to establish the possibility of stabilizing the carbocation linked with the η^5-cyclopentadienyl ligand in η^5-cyclopentadienyl-η^5 and (3)-1,2-dicarbollyliron(II). With this aim η^5-isopropenylcyclopentadienyl-η^5-(3)-1,2-dicarbollyliron(III) (I) was synthesized by us, its reduction into the Fe(II) form and its protonation have been studied. The synthesis of complex (I) was effected by the following scheme:



Isopropenylcyclopentadienylsodium (III) was obtained by the action of $NaNH_2$ in liquid NH_3 on 6,6-dimethylfulvene (II) and was reacted with 1,2-$C_2B_9H_{11}{}^{2-}Na_2{}^+$ and anhydrous $FeCl_2$. The resulting Na salt of η^5-isopropenylcyclopentadienyl-η^5-(3)-1,2-dicarbollyliron(II) (IV) was oxidized with H_2O_2 into complex (I) to purify it from other products and (I) was obtained in 34% yield. Complex (I) was a paramagnetic crystalline substance of a dark green color and was the first compound of this series containing a substituent in the η^5-cyclopentadienyl ring. Reduction of complex (I) with an excess of $NaBH_4$ in ethanol with subsequent treatment with Me_4NBr in water led practically quantitatively to the tetramethylammonium salt of η^5-isopropenylcyclopentadienyl-η^5-(3)-1,2-dicarbollyliron(II) (V) containing an Fe atom in the d^6 configuration.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2611-2615, November, 1983. Original article submitted January 17, 1983.

0568-5230/83/3211-2348$07.50