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SYNTHESIS OF PYRIDO[1,2-b][2,4]BENZODIAZEPIN-6(11H)-IMINES

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Condensation of o-bromomethylbenzonitrile and α-bromo-o-cyanophenylmethane with 2-aminopyridines gives 6-amino-6,11-dihydropyrido[1,2-b][2,4]benzodiazepines. Quaternary 2-aminopyridinium salts are intermediates in these reactions.

We have previously demonstrated that reaction of o-chloromethylbenzonitrile with 1-amino-3H-isoindole leads to the formation of a condensed derivative of a little-studied heterocyclic system, 2,4-benzodiazepine [1]. It was of interest to us to carry out the analogous conversion on 2-aminopyridine. This reaction is interesting from the point of view of synthesizing potentially neurotropic substances, such as those obtained via reaction of o-chloromethylbenzonitrile with anthranilic acid, for example [2].

Depending on the duration of reflux, two different compounds A and B can be obtained from an eqimolar mixture of o-bromomethylbenzonitrile (Ia) (experiments revealed that it was more convenient to work with this material rather than with o-chloromethylbenzonitrile Ib) with 2-aminopyridine IIa in acetonitrile.

Since IIa contains two sites which are receptive to electrophilic addition, namely, the ring nitrogen atom and the exocyclic amino group, the site of initial electrophilic attack will determine the structure of all of the possible subsequent products; it was therefore necessary to establish its structure by an independent pathway. It is not possible to determine this structure based on literature data, since it is known that the direction of alkylation of α-aminopyridine depends on the reaction conditions [3]. We have synthesized the quaternary salts IIIa,b starting from 2-bromopyridine; these were then treated with an excess of a saturated solution of ammonia in alcohol.

Treatment of quaternary salt IIIb results in the formation of 1-benzyl-2-aminopyridinium bromide IVb, while salt IIIa gives the quaternary salt IVa. Amination of salt IIIa does not result in loss of the nitrile group. A mixed melting point analysis of A and quaternary

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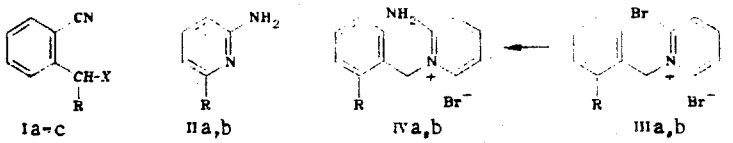
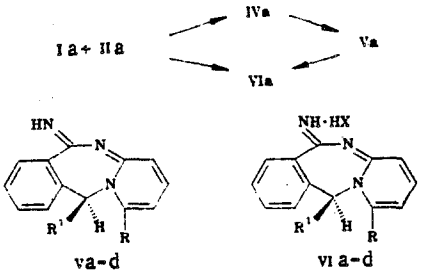


Ia-c IIa,b IVa,b IIIa,b

I a R=H, X=Br, b R=H, X=Cl, c R=Ph, X=Br; II a R=H, b R=Me; III, IV a R=CN, b R=H

salt IVa did not result in a mp depression; the IR spectra of the two substances also proved to be identical. Treatment of a solution of quaternary salt IVa with excess 2N NaOH at 20°C leads in high yield to a compound for which the structure 1-(2-cyanobenzyl)pyridin-2-imine might be proposed, except that the IR spectrum indicates the absence of the nitrile functional group; this, in turn, would seem to suggest that subsequent intramolecular cyclization at this group has occurred. Based on ^{13}C-NMR, PMR, UV, and IR spectral data we conclude that the base obtained in this manner has the structure 6-imino-6,11-dihydropyrido[1,2-b]-[2,4]benzodiazepine (Va). Treatment of comound Va with hydrobromic acid leads to the formation of the corresponding monohydrobromide derivative VIa, which, according to its IR spectrum and a mixed melting point determination, is identical with compound B obtained from Ia and IIa. Thus, short duration reflux of a mixture of 2-aminopyridine with o-bromomethylbenzonitrile gives the quaternary salt IVa, which, upon more extended reflux, undergoes intramolecular cyclization to give the hydrobromide derivative of 6-imino-6,11-dihydro[1,2-b][2,4]-benzodiazepine, VIa.



Va-d VIa-d

V a R=R^1=H; b R=Me, R^1=H; c R=H, R^1=Ph; d R=Me, R^1=R; VIa,c,d X=Br; b X=Cl

It was found that this two-stage method of pyridobenzodiazepine derivative preparation was not mandatory for other 2-aminopyridines and other compounds related to o-bromomethylbenzonitrile. Hydrobromides VIc, d, as well as hydrochloride VIb, were obtained in high yields in one step by refluxing equimolar amounts of the corresponding 2-aminopyridines IIa, b and halides Ia-c in acetonitrile. The observed differences in the course of reactions of compounds I and II are apparently associated with steric effects due to a methyl group in the 6-position in the starting base or to an α-phenyl ring in bromide Ic. The characteristic feature of the IR spectra of salts VIa-d is the complex frequency contour of the vibrational band associated with N–H stretching vibrations. This is probably the result of contributions from two protonated forms of amide fragments in the structure, which are responsible for the extremely broad frequency range of the N–H bond vibrations.

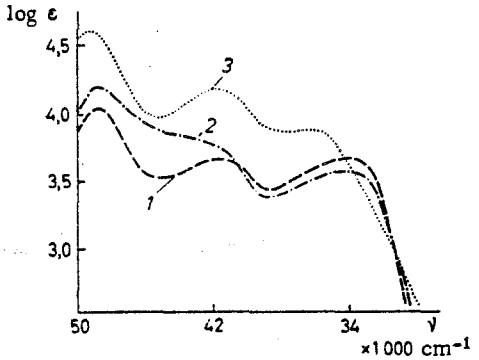


Fig. 1. Electronic spectra of salts: 1) VIa; 2) VIc; 3) VIII.

TABLE 1. Analytical and Spectral Data for Compounds III-VIII

Compound	IR spectrum, cm^{-1}			UV spectrum, λ_{max}, nm (log ε)	Found, %		Empirical formula	Calc., %	
	$\nu C\equiv N$	$\nu N-H$	$\nu C=C$ и $\nu C=N$		Hal	N		Hal	N
IIIa	2238		1615*, 1605, 1572, 1495, 1482, 1445	206 (4,17), 225 (3,91)*, 286 (3,75)	45,3	8,0	$C_{13}H_{10}Br_2N_2$	45,1	7,91
IIIb			1610, 1595, 1565, 1485, 1455, 1445	204 (4,29), 212 (4,18)*, 287 (3,90)	48,2	4,47	$C_{12}H_{11}Br_2N$	48,6	4,25
IVa	2220	3210, 3040	1655, 1630*, 1575, 1565, 1505, 1485, 1460, 1430	206 (4,20), 231 (4,13), 304 (3,64)	27,8	14,6	$C_{13}H_{12}BrN_3$	27,5	14,5
IVb		3220, 3030	1650, 1620*, 1575, 1520, 1490, 1465, 1445	204 (4,05), 235 (3,70), 310 (3,49)	29,9	10,4	$C_{12}H_{13}BrN_2$	30,1	10,5
Va		3243	1635, 1590, 1565, 1470, 1440, 1415	205 (4,28), 242 (4,00), 294 (3,96)		19,9	$C_{13}H_{11}N_3$		20,1
Vb		3242	1650, 1590, 1570, 1470, 1452, 1415	205 (4,37), 245 (3,98), 294 (4,05)		18,9	$C_{14}H_{13}N_3$		18,8
Vc		3240	1635, 1590, 1465, 1433	205 (4,30), 236 (3,90), 294 (3,76), 242 (3,85)*		14,8	$C_{19}H_{15}N_3$		14,7
Vd		3240	1640, 1590, 1575, 1470*, 1452	205 (4,35), 224 (4,09)*, 294 (3,89), 244 (3,85)		13,9	$C_{20}H_{17}N_3$		14,0
VIa		3480, 3420, 3340, 3020	1663, 1610, 1587, 1480, 1455, 1436	205 (4,01), 242 (3,67), 294 (3,66)	27,4	14,7	$C_{13}H_{12}BrN_3$	27,5	14,5
VIb		3440, 3380, 3120, 3030	1668, 1600, 1570, 1490, 1460, 1435*	206 (4,07), 247 (3,76), 295 (3,78)	13,4	16,3	$C_{14}H_{14}ClN_3$	13,6	16,2
VIc		3360, 3300, 3190, 3060	1665, 1595, 1573, 1483, 1458, 1440	205 (4,02), 238 (3,78), 294 (3,58)	21,8	11,7	$C_{19}H_{16}BrN_3$	21,8	11,5
VId		3400, 3160, 3000	1675, 1600, 1570, 1490, 1460, 1445*	207 (4,50), 247 (3,58), 296 (3,62)	21,2	11,2	$C_{20}H_{18}BrN_3$	21,0	11,0
VIb		3283	1628, 1590, 1495, 1458, 1408	205 (4,26), 238 (3,92), 283 (3,60)		13,5	$C_{14}H_{12}N_2$		13,4
VIII		3490, 3430, 3200, 3070	1675, 1620, 1590, 1495, 1576, 1455	204 (4,59), 241 (4,18), 277 (3,88)	27,3	9,83	$C_{14}H_{13}BrN_2$	27,6	9,69

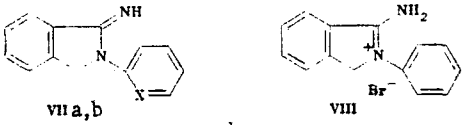
*The inflection point in the absorption curve.

The PMR spectra of salts IVa-d exhibit sharp signals for the protons of the pyridine portion of the tricyclic system and for the protons attached to the $C_{(11)}$ carbon atom. The phenyl substituent attached to $C_{(11)}$ in compounds IVc,d appears in the spectrum as a multiplet. The 7-H proton, due to nonbonded interaction with the neighboring amino group, absorbs downfield relative to the other aromatic protons. The PMR spectra of salts VIa-d (in DMSO-D_6) contain two broadened signals for the N–H protons, which disappear after addition of D_2O to the sample. The electronic absorption spectra of salts VIa,c are shown in Fig. 1 and are characterized by the presence of three absorption bands.

Treatment of aqueous solutions of salts VIa-d with excess 2 N alkali leads to the formation of neutral bases Va-d in nearly quantitative yields; the latter compounds have substantially lower melting points than the corresponding salts (cf. Table 1). The IR spectra of bases Va-d are characterized by significant simplification of the absorption contour in the 3200 cm^{-1} region in comparison with salts VIa-d; they contain narrow, medium intensity bands

due to =N–H stretching vibrations (see Table 1). The absorption contour in the electronic spectra of bases Va-d is somewhat more complex, due to the appearance of many inflection points in the curves. The PMR spectra contain singlet signals for the phenyl substituent protons at $C_{(11)}$. In addition, a signal for the imino group proton in the 6-position of the ring system is found in the spectra of bases Va-d.

Although the cyclization of quaternary salt IVa to give the 6-imino derivative Va proceeds under mild conditions, we wanted to explore the possibility of the occurence of a Dimroth rearrangement, which would lead to the formation of 2-(2-pyridyl)isoindolin-1-imine VIIa. Compound VIIa has not been reported in the literature. For this reason, we compared the spectral characteristics of imine Va with the relatively more accessible imine derivative VIIb [4], which was prepared from bromide VIII (Table 1, Fig. 1). Analysis of the data confirmed that the indicated condensation reaction does in fact lead to the formation of [2,4]-benzodiazepine rings. Furthermore, we also studied the effects of lanthanide shift reagents (LSR), namely, $Eu(FOD)_3$ and $Eu(DPM)_3$, which are well known for their ability to coordinate efficiently with pyridine type nitrogen atoms [5].



VII a,b VIII

VII a X=N; b X=CH

It was found that the indicated shift reagents did not give any definitive lanthanide induced shifts (LIS) with bases Va,c. This is qualitative proof of the validity of our conclusions.

It should also be noted that quaternary salt IVa has been noted previously in the literature, with physical constants different from those obtained herein, in a study [6] of the synthesis of pyrido[1,2-b][2,4]benzodiazepin-6(11H)-one and its hydrogenated derivatives.

EXPERIMENTAL

Melting points were measured on a heated Böetius stage. UV spectra were obtained for $2 \cdot 10^{-5}$ M solutions of the indicated substances in ethanol solution using a Specord UV-Vis spectrophotometer. IR spectra were recorded on a Pye Unicam SP3-300 spectrophotometer for KBr pellets. ^{13}C-NMR and PMR spectra were measured on Bruker WP-100SY and CPX-200 spectrometers versus TMS as internal standard on the δ scale.

o-Bromomethylbenzonitrile Ia was prepared according to [7], o-chloromethylbenzonitrile Ib according to [3], and α-bromo-o-benzonitrile Ic according to [8].

Condensation of o-Bromomethylbenzonitrile with 2-Aminopyridine. A mixture of 2.07 g (22 mmole) of 2-aminopyridine and 4.35 g (22 mmole) o-bromomethylbenzonitrile in 10 ml acetonitrile was refluxed for 1 min, cooled, and the resulting precipitate was filtered. Yield 3.3 g (51%) of colorless crystals, mp 251-252°C (from aqueous 2-propanol). [Substance A, 2-amino-1-(2-cyanobenzyl)pyridinium bromide]. The filtrate was refluxed for 1 h and 30 min and gave, after cooling, 2.85 g (44%) of crystalline substance B, 6-imino-6,11-dihydro[1,2-b]-[2,4]benzodiazepine hydrobromide, mp 293-294°C (from aqueous 2-propanol).

2-Bromo-1-benzylpyridinium Bromide (IIIb). A mixture of 4.4 ml (50 mmole) 2-bromopyridine, 5.9 ml (50 mmole) benzyl bromide, and 10 ml acetonitrile was refluxed for 20 h. The mixture was then allowed to stand at 20°C for 20 days, after which the resulting precipitate was filtered. Yield 5.8 g (36%), mp 193°C (from 2-propanol–water). PMR spectrum (CF_3COOD): 5.47 (2H, s, N–CH_2), 7.07 (1H, d, J = 7.5 Hz, 3-H), 8.05 ppm (1H, d, J = 6 Hz, 6-H).

2-Bromo-1-(2-cyanobenzyl)pyridinium Bromide (IIIa). A mixture of 9.8 g (50 mmole) o-bromomethylbenzonitrile, 4.4 ml (50 mmole) 2-bromopyridine, and 15 ml acetonitrile was refluxed for 20 h. After 20 days 4.8 g (65%) of a colorless salt crystallized in the mixture and was removed and recrystallized from a 2-propanol–water mixture to give crystals, mp 167-168°C. PMR spectrum (CF_3COOD): 6.39 (2H, s, N–CH_2); 7.37 (1H, d, J = 7.5 Hz, 3-H); 9.16 ppm (1H, d, J = 6 Hz, 6-H).

2-Amino-1-benzylpyridinium Bromide (IVb). To 5 g (15 mmole) 2-bromo-1-benzylpyridinium bromide at 20°C was added a twofold excess of either 12% aqueous ammonia or a saturated ammonia alcohol solution. The starting salt dissolves initially, and after 5 h a new precipitate begins to form. The reaction mixture was maintained an additional 12 h at 20°C, the

precipitate was filtered and washed with acetone. Yield 30.5 g (76%), mp 205°C (from aqueous 2-propanol). PMR spectrum (CF_3COOD): 6.05 (2H, s N–CH_2), 8.90 ppm (1H, d, J = 6.2 Hz, 6-H).

2-Amino-1-(2-cyanobenzyl)pyridinium Bromide (IVa). To 0.5 g (1.4 mmole) salt IIIa, which was cooled externally with ice, was added 15 ml of saturated ammoniacal alcohol solution. The solid salt dissolves and after a few minutes the solution turns orange. The reaction mixture was maintained at 5°C for 1 day and then the resulting precipitate was removed by filtration. Yield 0.23 g (56%) of orange crystals, mp 251-255°C (from aqueous 2-propanol); according to [5], mp 239-240°C. A mixed melting point probe of bromide IVa and substance A, prepared by condensation of compounds Ia and IIa, did not give a mp depression. The two materials also had identical IR spectra. PMR spectrum (CF_3COOD): 5.80 (2H, s, N–CH_2), 7.0-7.48 (3H, m,), 7.57-8.12 ppm (5H, m).

6-Imino-6,11-dihydropyrido[1,2-b][2,4]benzodiazepine (Va). Salt IVa (2.9 g, 10 mmole) was dissolved at 20°C in 10 ml water and 5 ml 2 N NaOH solution was added. The resulting precipitate was filtered and washed with water to a neutral point. After drying 1.8 g (86%) of a colorless amorphous substance was obtained, mp 138°C (from 2-propanol). ^{13}C-NMR spectrum ($CDCl_3$): 161.7 ($C_{(6)}$); 154.2 ($C_{(4a)}$); 138.2 ($C_{(6a)}$); 134.0 ($C_{(10a)}$); 147.2 ($C_{(1)}$); 137.4 ($C_{(3)}$); 127.7 ($C_{(4)}$); 122.4 ($C_{(8)}$); 122.0 ($C_{(9)}$); 117.2 ($C_{(7)}$); 111.9 ($C_{(10)}$); 51.8 ($C_{(11)}$). PMR spectrum ($CDCl_3$): 4.99 (2H, s, 11-CH_2); 8.38 (1H, d, J = 5.5 Hz, 1-H); 6.95 (1H, q, $J_{1,2}$ = 5.5, $J_{2,2}$ = 7.5 Hz, 2-H); 7.39-7.91 (6H, m, arom).

6-Imino-6,11-dihydropyrido[1,2-b][2,4]benzodiazepine Hydrobromide (VIa). This was formed by passing gaseous hydrogen bromide through an alcohol solution of Va. The resulting hydrobromide salt precipitate was removed by filtration and recrystallized from 2-propanol, mp 293-294°C (dec). A mixed melting point determination with substance B, prepared by condensation of 2-aminopyridine and o-bromoethylbenzonitrile, gave mp 292-294°C. The IR spectra of the two materials were also identical. PMR spectrum (CF_3COOD): 5.29 (2H, s, 11-CH_2); 8.96 (1H, d, J = 5.5 Hz, 1-H); 8.64 (1H, t, J = 8 Hz, 3-H); 8.32 (1H, d, J = 7.5 Hz, 4-H); 8.23 (1H, d, J = 8 Hz, 7-H); 8.11 (1H, t, J = 7.5 Hz, 8-H); 8.04 (1H, q, J = 5.5 Hz, 2-H); 2.93 ppm (1H, d, J = 7.5 Hz, 10-H).

6-Imino-11-phenyl-6,11-dihydropyrido[1,2-b][2,4]benzodiazepine Hydrobromide (VIc). A mixture of 0.94 g (10 mmole) 2-aminopyridine and 2.72 g (10 mmole) α-bromo-1-benzylbenzonitrile in 10 ml acetonitrile was refluxed for 5 h. After cooling to 20°C the reaction mixture deposited 2.93 g (80%) of colorless crystals, mp 299-301°C (from DMF). PMR spectrum (CF_3COOD): 8.99 (1H, d, J = 5.5 Hz, 1-H); 8.61 (1H, t, J = 7.8 Hz, 3-H); 8.42 (1H, d, J = 8 Hz, 4-H); 7.01 (1H, t, J = 7.5 Hz, 9-H); 8.10 (1H, d, J = 7.5 Hz, 7-H); 6.92 ppm (1H, s, 11-H).

6-Imino-1-methyl-6,11-dihydropyrido[1,2-b][2,4]benzodiazepine Hydrochloride (VIb). This was obtained by condensation of equimolar amounts of 2-amino-6-methylpyridine IIb with o-chloromethylbenzonitrile, in 66% yield, under conditions identical to those described above for compound VIc. Mp 274°C (from 2-propanol). PMR spectrum ($DMSO-D_6$): 5.47 (2H, s, 11-CH_2); 2.60 (3H, s, 1-Me); 8.84 (1H, d, 7-H); 8.00 (1H, t, 8-H); 7.39 (1H, d, J = 7.5 Hz, 2H); 7.28 (1H, d, J = 7.5 Hz, 4-H); 11.88 and 11.11 ppm (s, N–H).

6-Imino-1-methyl-11-phenyl-6,11-dihydropyrido[1,2-b][2,4]benzodiazepine Hydrobromide (VId). This was prepared in 95% yield by condensation of equimolar amounts of compounds IIb and bromide Ia under conditions identical to those described above for compound VIc, mp 319°C (from 2-propanol). PMR spectrum ($DMSO-D_6$): 7.18 (1H, s, 11-H); 2.16 (3H, s, 1-Me); 8.68 (1H, d, J = 7 Hz, 7-H); 7.36 (5H, s, 11-Ph); 7.79 (1H, t, J = 7 Hz, 8-H); 11.24 and 11.08 ppm (s, N–H).

6-Imino-11-phenyl-6,11-dihydropyrido[1,2-b][2,4]benzodiazepine (Va). This was prepared in 74% yield by treatment of an aqueous solution of salt VIc with excess 2 N NaOH solution, mp 213°C (from 2-porpanol). PMR spectrum ($CDCl_3$): 6.27 (1H, s, 11-H); 8.30 (1H, d, J = 5.5 Hz, 1-H); 7.92 (1H, m, 3-H); 6.84 (1H, q, $J_{1,2}$ = 5.5, $J_{2,3}$ = 7.5 Hz, 2-H); 7.25 (5H, s, 11-Ph). ^{13}C-NMR spectrum ($CDCl_3$): 161.1 ($C_{(6)}$); 153.3 ($C_{(4a)}$); 143.3 ($C_{(6a)}$); 132.6 ($C_{(11)}$); 147.0 ($C_{(1)}$); 136.8 ($C_{(3)}$); 130.9 ($C_{(2)}$); 128.5 ($C_{(11)}$); 127.7 ($C_{(4)}$); 127.4 ($C_{(11)}$); 126.0 ($C_{(11)}$); 122.5 ($C_{(8)}$); 122.1 ($C_{(9)}$); 117.1 ($C_{(7)}$); 113.1 ($C_{(10)}$); 65.9 ppm ($C_{(11)}$).

6-Imino-1-methyl-6,11-dihydropyrido[1,2-b][2,4]benzodiazepine (Vb). Yield 94% via treatment of an aqueous solution of compound VIb with excess 2 N alkali, mp 148-149°C (from

2-propanol). PMR spectrum (DMSO-D_6): 2.46 (3H, s, 1-Me); 5.01 (2H, s, 11-CH_2); 6.90 (1H, d, J = 7.5 Hz, 2-H); 7.96 (1H, m, 3-H); 8.66 ppm (1H, br s, N–H).

6-Imino-1-methyl-11-phenyl-6,11-dihydropyrido[1,2-b][2,4]benzodiazepine (Vd). Yield 95% upon treatment of an aqueous solution of salt VId with excess 2 N alkali, mp 201-202°C (from 2-propanol). PMR spectrum (DMSO-D_6): 2.36 (3H, s, 1-Me); 6.56 (1H, s, 11-H); 6.81 (1H, d, J = 7.5 Hz, 2-H); 7.26 (5H, s, 11-Ph); 7.97 ppm (1H, m, 3-H).

1-Amino-2-phenyl-3H-isoindole Hydrobromide (VIII). This was prepared according to [4] from aniline and α-bromo-o-toluinitrile. PMR spectrum (CF_3COOD): 5.28 (2H, s, 3-CH_2); 8.24 (1H, d, J = 7.5 Hz, 7-H); 7.45-8.02 ppm (8H, m, arom).

1-Imino-2-phenylisoindoline (VIIb). This was obtained from salt VIII according to [4]. mp 134°C (from 2-propanol); according to literature data, mp 121°C (from aqueous alcohol). PMR spectrum ($CDCl_3$): 4.84 (2H, s, 3-CH_2); 6.72 (1H, br s, N–H); 7.76 (3H, d, 7- and 2-H); 7.06-7.55 ppm (6H, m). ^{13}C-NMR spectrum ($CDCl_3$): 162.8 ($C_{(1)}$); 140.3 ($C_{(2)}$); 138.2 ($C_{(7a)}$); 133.6 ($C_{(3a)}$); 130.3 ($C_{(7)}$); 128.09 ($C_{(2)}$); 127.5 ($C_{(4)}$); 123.4 ($C_{(2)}$); 122.2 ($C_{(6)}$); 121.6 ($C_{(5)}$); 120.6 ($C_{(2)}$); 53.3 ppm ($C_{(3)}$).

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SYNTHESIS AND STRUCTURE OF HYDROXYISOXAZOLIDINES AND DERIVATIVES OF HYDROXYLAMINE AND ALKENALS

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The reactions of N-substituted hydroxylamines with alkenals serve as a method for the synthesis of the corresponding 2-substituted 3(5)-hydroxyisoxazolidines. The reaction pathway is determined by the nature of the substituent attached to the nitrogen atom. Ring–chain isomerism has been detected in these newly obtained compounds

Only isolated reports have been published concerning the synthesis of hydroxy derivatives of isoxazolidines. The preparation of several 2-aryl-5-hydroxy- [1, 2] and 2-acyl-3-hydroxyisoxazolidines [3-5] via treatment of alkenals with hydroxylamine derivatives has been described, although in most cases the structures of the products were not rigorously proved. The present paper deals with a systematic study of the condensation reactions of hydroxylamine derivatives with α,β-unsaturated aldehydes.

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