5-Amino-4,5-dihydroisoxazoles. Part I. 5-Amino-3-aryl-4-methylene-4,5-dihydroisoxazoles and 4-Aminomethyl-3-arylisoxazoles from 5-Amino-4-aminomethyl-3-aryl-4,5-dihydroisoxazoles

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5-Amino-4-aminomethyl-3-aryl-4,5-dihydroisoxazoles **2** were obtained by cycloaddition of nitrile oxides to 1,3-diaminopropenes **1**. On reaction with methyl iodide the corresponding 4-(quaternary)-ammoniomethyl iodides **3** were formed. These compounds, on reaction with bases, afforded 5-amino-3-aryl-4-methylene-4,5-dihydroisoxazoles **4**. The acid-catalyzed deamination of compounds **2** afforded 4-aminomethyl-3-arylisoxazoles **5** and 3-arylisoxazoles as retro-Mannich products. The deamination of **2** to yield **5** was also obtained by base catalysis.

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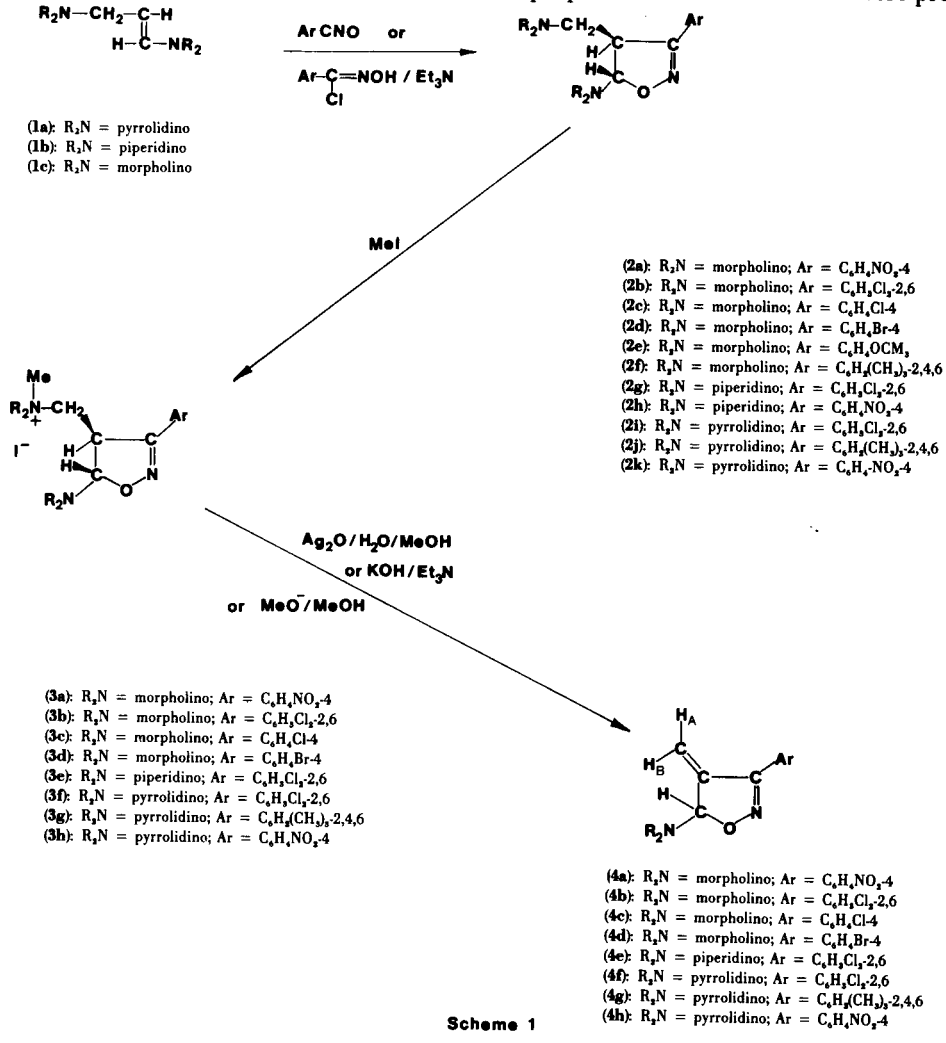
In previous work we prepared several 5-amino-4-aminomethyl-1-aryl-4,5-dihydro-*v*-triazoles. These compounds showed an interesting behaviour in the acid- and base-catalyzed deamination reactions (1) and represented a satisfactory entry to 5-amino-4-methylene-4,5-dihydro-*v*-triazoles, which are of interest both for their isomerization reactions and for their reactivity with nucleophiles (2).

In the context of our general interest in the preparation and chemistry of aminomethyl- and methylene-substituted amino-4,5-dihydroazoles, we now report some of our results in the isoxazole series. The 5-amino-4-aminomethyl-3-aryl-4,5-dihydro-isoxazoles **2a-k** were prepared by cycloaddition of nitrile oxides to the *trans*-1,3-diaminopropenes **1a-c**. The enamines were produced according to



Scheme 1

0022-152X/80/050881-05$02.25

the method of Mannich (3) from acrolein and secondary amines. Their *trans* configuration is confirmed by the vinylic coupling constant of 13.5 Hz in the ^{1}H-nmr spectrum. The less stable nitrile oxides were generated *in situ* from the corresponding benzohydroxamoyl chlorides with triethylamine; the more stable ones (mesitonitrile oxide and 2,6-dichlorobenzonitrile oxide) were reacted in the isolated form.

The structures of compounds **2a-k** were confirmed by analytical and spectral data and their properties are listed in Table 1. In the ^{1}H-nmr spectra the coupling constants between H-4 and H-5 have a value of 2-3 Hz and of 4.4-4.8 Hz for compounds **2a,c-e,h,k** and for compounds **2b,f,g,i,j**, respectively (4). These values confirm in both cases the *trans* configuration of the 4,5-dihydroisoxazoles (6,7,8).

By reacting compound **2** with a slight excess of methyl iodide in acetonitrile and at room temperature, the corresponding quaternary ammonium iodides **3a-h** could be prepared. With the less nucleophilic morpholine derivatives the reaction was complete only after several days, but the mild conditions employed were necessary to avoid reaction at both amino substituents. The constitution of compounds **3a-h** was easily confirmed by analysis and the site of quaternarization was inferred from the ^{1}H-nmr spectra which showed a remarkably downfield shift of the signal associated with the methylene protons, with respect to the corresponding **2**. The properties of compounds **3a-h** are listed in Table 2 (9).

On tertiary amine elimination compounds **3a-h** afforded the corresponding 4-methylene-4,5-dihydroisoxazoles **4a-h**. They represent a new class of compounds (10). The elimination was performed by one or more of the following methods. (a) With silver oxide in moist methanol or ethanol. Satisfactory yields in a short reaction time were always obtained. (b) With potassium hydroxide in triethylamine. This reagent required long reaction times, but in some instances was superior to method (a) yielding very pure reaction products which were insoluble in the reaction medium and could be easily recovered. (c) With sodium methoxide in methanol. This procedure gave no problems when applied to substrates **3b** and **3g**, yielding a single reaction product. However, from **3a** a mixture of the expected **4a** and of its reaction products with methoxide (12) was obtained.

The structure of the 5-amino-4-methylene-4,5 dihydroisoxazoles **4a-h** was confirmed by analytical and ^{1}H-nmr criteria. The relevant data are listed in Table 3. In the ^{1}H-nmr spectra of compounds **4b,e-g** the $CH_2{=}\overset{|}{C}{-}CH$ system is associated with an ABX pattern with $J_{AB} \cong 0$ Hz. Such patterns have been already described for similar structures (11,14). The lower field signal was associated to H-5, since it is linked to a carbon atom bearing two electronegative substituents. This assignment is also confirmed by the fact that it is the more influenced by protonation. The higher field signal was related to H_A because it should be more shielded by the bulky aromatic substituent which is obliged in a conformation perpendicular to the dihydroisoxazole ring (as shown by molecular models).

In the ^{1}H-nmr spectra of **4a,c,d**, the signals associated with H_A and H_B are shifted to lower field and show almost identical values. This can be explained by the greater conformational freedom of the aryl substituent which can attain co-planarity with the isoxazole ring, allowing a conjugative effect, which is indirectly extended to the methylene group. This results in a deshielding effect which is more evident in **4a**.

The results obtained with lanthanide induced shifts

Table 1

trans-5-Amino-4-aminomethyl-3-aryl-4,5-dihydroisoxazoles **2**

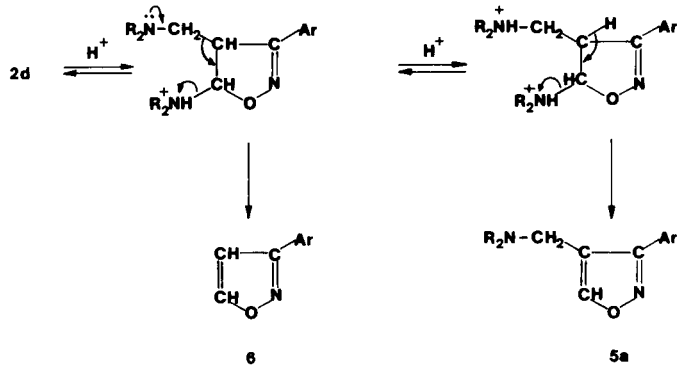
Compound No.	Recristalliz-ation Solvent	M.p. (°C)	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N	^{1}H-Nmr (Deuteriochloroform) $\delta_{H\text{-}4}$[a]	$\delta_{H\text{-}5}$	$J_{4\text{-}5}$
2a	ethanol	179-181	70	57.7	6.2	14.6	$C_{18}H_{24}N_4O_5$	57.5	6.4	14.9	~3.65	5.33	2.3
2b	isopropyl alcohol	171-172	80	54.3	5.8	10.7	$C_{18}H_{23}Cl_2N_3O_3$	54.0	5.8	10.5	~3.75	5.07	4.5
2c	ethanol	133-135	30	59.3	6.5	11.3	$C_{18}H_{24}ClN_3O_3$	59.1	6.6	11.5	~3.6	5.38	3
2d	ethanol	135	75	52.8	6.0	10.2	$C_{18}H_{24}BrN_3O_3$	52.7	5.9	10.3	~3.5	5.21	2
2e	isopropyl ether/ isopropyl alcohol	152	20	62.9	7.4	11.6	$C_{19}H_{27}N_3O_4$	63.2	7.55	11.6	~3.65	5.36	2.3
2f	isopropyl ether	115-118	45	67.4	8.3	11.5	$C_{21}H_{31}N_3O_3$	67.6	8.4	11.3	~3.6	5.12	4.8
2g	isopropyl ether	115-118	50	60.8	6.9	10.5	$C_{20}H_{27}Cl_2N_3O$	60.6	6.85	10.6	3.69	5.02	4.4
2h	(b)	136-138	30	64.3	7.9	14.8	$C_{20}H_{28}N_4O_3$	64.5	7.6	15.1	3.52	5.34	2.7
2i	*n*-pentane	105-109	65	58.8	6.35	11.4	$C_{18}H_{23}Cl_2N_3O$	58.7	6.3	11.4	3.67	5.50	4.4
2j	*n*-pentane	95-98	75	73.8	9.4	12.2	$C_{21}H_{31}N_3O$	73.9	9.15	12.3	3.62	5.62	4.7
2k	methanol	132-134	20	62.5	7.3	16.2	$C_{18}H_{24}N_4O_3$	62.8	7.0	16.3	3.57	5.78	2.7

(a) Signals for which approximate values are given partially overlapped by the amine signals. (b) Purified by column chromatography with benzene/ethyl acetate 2:3.

with $Eu(fod)_3$ are in agreement. In the case of **4g**, the signal associated with H_B suffered a greater downfield shift with respect to the signal related to H_A. Accordingly, in the presence of $Eu(fod)_3$ the ABC pattern observed for **4a** was resolved to the expected ABX pattern.

The amine elimination from 5-amino-4,5-dihydroisoxazoles to yield the corresponding aromatic isoxazoles has been generally catalyzed by acids (15). By refluxing with hydrochloric acid in 95% ethanol solution, the 4,5-dihydroisoxazole (**2d**) afforded the expected 3-(4-bromophenyl)-4-morpholinomethylisoxazole (**5a**) together with a substantial amount of 3-(4-bromophenyl)-isoxazole (**6**).

Under the same conditions, compound **2b** afforded a complex mixture of at least four products in which 3-(2,6-dichlorophenyl)-4-morpholinomethylisoxazole and 3-(2,6-dichlorophenyl)isoxazole could be identified (by ^{1}H-nmr), but no effort was made for their isolation. The formation of the 4-unsubstituted isoxazole derivatives can be rationalized as a retro-Mannich reaction (16) occurring on the protonated **2** as shown in Scheme 2 (18).



Scheme 2

To avoid the formation of deaminomethylation products the aromatization of compounds **2a,c,d** was attempted under basic conditions. The compounds **2a,c,d** (Scheme 3) were refluxed with sodium hydroxide in methanol. Under these conditions the reaction was slow and afforded

Table 2

Quaternary Ammonium Iodides **3**

Compound No.	Recrystallization Solvent	M.p. (°C)	Yield (%)	Found (%) C	H	N	Formula	Required (%) C	H	N
3a	ethanol	181-183	65	44.0	5.2	10.8	$C_{19}H_{27}IN_4O_5$	44.0	5.3	10.8
3b	acetonitrile/ethyl ether	187-190	80	41.3	4.9	10.0	$C_{19}H_{26}Cl_2IN_3O_3$	41.0	4.7	10.1
3c	chloroform/ethyl ether	175-177	50	44.7	5.0	8.0	$C_{19}H_{27}ClIN_3O_3$	45.0	5.4	8.3
3d	chloroform	177-181	80	41.0	4.9	7.4	$C_{19}H_{27}BrIN_3O_3$	41.3	5.0	7.6
3e	ethyl ether (a)	139-141	81	46.5	5.4	7.7	$C_{21}H_{30}Cl_2IN_3O$	46.9	5.6	7.8
3f	acetonitrile/*n*-pentane	138-140	70	44.7	4.9	8.2	$C_{19}H_{26}Cl_2IN_3O$	44.7	5.2	8.3
3g	ethanol	195-198	55	54.6	6.9	8.7	$C_{22}H_{34}IN_3O$	54.7	7.1	8.7
3h	acetonitrile	160-162	60	47.2	5.3	11.6	$C_{19}H_{27}IN_4O_3$	46.9	5.6	11.5

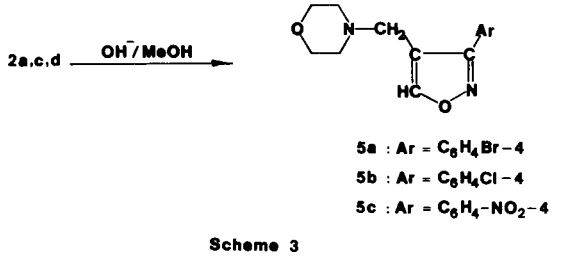
(a) Purified by extraction with ethyl ether.

Table 3

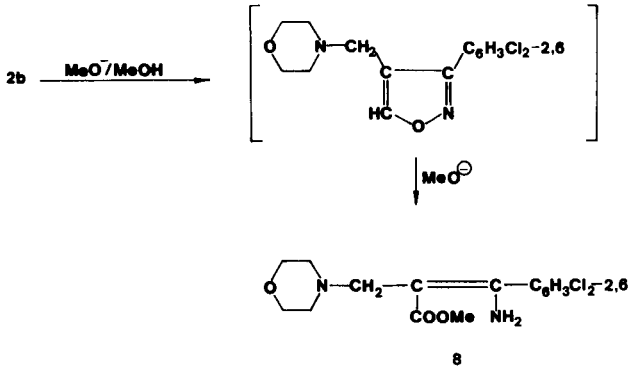
5-Amino-3-aryl-4-methylene-4,5-dihydroisoxazoles **4**

Compound No	Recrystallization Solvent	m.p. (°C)	Method	Yield	Found (%) C	H	N	Formula	Required (%) C	H	N	Solvent	^{1}H-Nmr δ H-A	δ H-B	δ H-5	J 5-A	J 5-B
4a	ethanol	123-125	a	35	58.3	5.5	14.3	$C_{14}H_{15}N_3O_4$	58.1	5.2	14.5	benzene-d_6	5.13	5.21	5.42	2.8	2.5 (a)
			b	80								deuteriochloroform	5.59	5.59	5.45		
			c	35													
4b	benzene/ethyl ether	142-143	a	85	53.9	4.8	8.5	$C_{14}H_{14}Cl_2N_2O_2$	53.7	4.5	9.0	acetone-d_6	5.36	5.59	6.09	3.2	2.8
	or ethanol		b	45								deuteriochloroform	5.14	5.36	5.78	3.1	2.7
			c	25													
4c	isopropyl ether	99-101	a	30	60.1	5.6	9.8	$C_{14}H_{15}ClN_2O_2$	60.3	5.4	10.1	deuteriochloroform	5.94	5.94	5.62	—	—
4d	isopropyl alcohol	98-101	a	35	52.3	4.7	8.7	$C_{14}H_{15}BrN_2O_2$	52.0	4.7	8.7	deuteriochloroform	5.79	5.79	5.62	—	—
												benzene-d_6	5.13	5.26	5.38	—	—
4e	*n*-pentane	75-77	a	30	57.7	5.1	9.0	$C_{15}H_{16}Cl_2N_2O$	57.9	5.2	9.0	deuteriochloroform	5.20	5.45	5.93	3.1	2.8
4f	hexane or isopropyl ether	93-95	b	70	56.6	4.5	9.1	$C_{14}H_{14}Cl_2N_2O$	56.6	4.8	9.4	deuteriochloroform	5.07	5.36	6.10	3.4	2.8
4g	hexane	79-81	a	80	75.3	8.0	10.2	$C_{17}H_{22}N_2O$	75.5	8.2	10.4	deuteriochloroform	5.02	5.31	6.01	3.1	2.8
			c	50													
4h	ethanol	93	b	85	61.4	5.5	15.1	$C_{14}H_{15}N_2O_3$	61.5	5.6	15.4	deuteriochloroform	5.70	5.81	6.22	2.8	2.5

(a) Spectrum not first order; J values confirmed by recording in the presence of $Eu(fod)_3$.



Scheme 3



Scheme 4

the expected products in 40-70% yield. The formation of some by products can be explained by the known lability to basic reagents of the isoxazole nucleus. This is confirmed by the behaviour of compound **2b** which did not react significantly with sodium hydroxide in methanol. Prolonged heating with sodium methoxide in methanol afforded the enamine **8** whose formation can be explained through nucleophilic ring cleavage (19) (Scheme 4).

EXPERIMENTAL

Melting points are uncorrected. ^{1}H-nmr spectra were recorded with Varian A-60 and 360-A spectrometers operating at 60 MHz (TMS as internal standard); silica gel (Merck) was used for column chromatography; tlc was run on silica gel (GF 254, Merck) with benzene (10-60%)-ethyl acetate as eluent.

4-Nitro-, 4-chloro- and 4-bromobenzohydroxamoyl chloride were prepared by reacting the corresponding aldoximes with *N*-chlorosuccinimide at room temperature and in chloroform. 2,4,6-Trimethyl- and 2,6-dichlorobenzonitrile oxide were obtained according to the literature (20).

5-Amino-4-aminomethyl-3-aryl-4,5-dihydroisoxazoles (**2**).

a)

The enamine **1** (10 mmoles) was dissolved in anhydrous acetonitrile (50 ml.) and triethylamine (10 mmoles) was dropped in. To the stirred solution the benzohydroxamoyl chloride (10 mmoles) was added. Stirring was continued for 2-5 hours at room temperature and thereafter the solvent was evaporated *in vacuo* at 30-35°. The residue was taken up in chloroform (50-100 ml.) and the solution was washed with water, dried over sodium sulphate and evaporated. The residue was recrystallized.

b)

The enamine **1** (10 mmoles) was dissolved in anhydrous benzene or anhydrous acetonitrile (25-50 ml.). The solid benzonitrile oxide was added under stirring. After 24-48 hours at room temperature the reaction mixture was evaporated to dryness and the residue was recrystallized or purified by column chromatography.

Yields and physical properties of the products **2** are listed in Table 1.

Quaternary Ammonium Iodides (**3**).

The 4,5-dihydroisoxazole **2** (5 mmoles) was dissolved in the minimum amount of anhydrous acetonitrile and methyl iodide was added (6 mmoles). The reaction solution was stirred at room temperature and the progress of the quaternarization was checked by tlc. When a solid precipitate was obtained, it was filtered out directly. For the more soluble products the solution was evaporated to dryness leaving a viscous residue which generally could be solidified by adding diethyl ether. After filtration the product was washed with diethyl ether and recrystallized. Yields and physical properties of compounds **3** are contained in Table 2.

5-Amino-3-aryl-4-methylene-4,5-dihydroisoxazoles (**4**).

a)

Compound **3** (5 mmoles) was suspended or dissolved in methanol (20 ml.) and silver oxide (7 mmoles) was added. The suspension was stirred at room temperature until complete reaction (tlc). The reaction mixture was then filtered with suction and the filtrate was evaporated to dryness. The residue was recrystallized yielding pure product **4**.

b)

The starting material **3** (5 mmoles) was suspended in triethylamine (40 ml.) which had been previously shaken with moist potassium hydroxide pellets. The reaction mixture was stirred at 40° until complete elimination (checked by tlc). A precipitate was generally formed and was isolated by filtration yielding a first crop of the product. The mother liquor (or the whole reaction mixture when a precipitate was not directly obtained) was evaporated and the residue taken up with benzene and filtered. The filtrate was washed with water until neutral and dried over sodium sulphate. After evaporation the residue was recrystallized.

c)

The quaternary ammonium iodide **3** (5 mmoles) was dissolved in methanol (100 ml.) and sodium methoxide (10 mmoles) in methanol (5 ml.) was added. The reaction mixture was stirred at room temperature for 48 hours or until disappearance of the starting material (tlc). A precipitate was formed in some instances. The reaction mixture was then evaporated to dryness, taken up with water (50 ml.) and filtered. The solid residue was dissolved in benzene and the solution washed with water and evaporated. The residue was recrystallized until pure. The mother liquor of the recrystallization was evaporated and chromatographed on a silica gel column yielding another crop of product **4**. Yields and physical properties of compounds **4** are described in Table 3.

Reaction of **2d** with Hydrochloric Acid/Ethanol.

Compound **2d** (1.5 g., 3.66 mmoles) was dissolved in ethanol (40 ml.) and 37% hydrochloric acid (0.7 ml.) was dropped in. The reaction mixture was refluxed for 12 hours. The solvent was evaporated and the residue taken up with water and chloroform (20 + 20 ml.). The organic layer was washed with 5% sodium hydrogen carbonate and evaporated. The residue was chromatographed with ethyl acetate/benzene (3:2) as eluent yielding **6** (0.2 g., 25%) as white crystals (from *n*-pentane/isopropyl ether, 1:1), m.p. 97-99° (lit. (21) m.p. 101°). The second fraction yielded compound **5a** (0.6 g., 50%) as white crystals (from methanol), m.p. 119-121°; nmr (deuteriochloroform): 3.38 (2H, s, CH_2), 8.41 (1H, s, H-5).

Anal. Calcd. for $C_{14}H_{15}BrN_2O_2$: C, 52.0; H, 4.7; N, 8.7. Found: C, 51.9; H, 4.7; N, 8.6.

Reaction of **2a,c,d** with Sodium Hydroxide/Methanol.

The dihydroisoxazole **2** (3 mmoles) was dissolved in methanol containing 1% sodium hydroxide (50 ml.). The mixture was refluxed for 12-30 hours. The solvent was evaporated, the residue dissolved in chloroform (25 ml.) and the organic phase washed until neutral with water.

After evaporation, the crude product was recrystallized.

Compound **5a**.

This compound had m.p. 119-120°, yield 40%.

Compound **5b**.

This compound had m.p. 117-119° (from isopropyl ether), yield 50%; nmr (deuteriochloroform): 3.34 (2H, s, CH_2), 8.25 (1H, s, H-5).

Anal. Calcd. for $C_{14}H_{15}ClN_2O_2$: C, 60.3; H, 5.4; N, 10.1. Found: C, 60.0; H, 5.1; N, 9.8.

Compound **5c**.

This compound had m.p. 121-124° (from ethanol), yield 70%; nmr (deuteriochloroform): 3.38 (2H, s, CH_2); 8.37 (1H, s, H-5).

Anal. Calcd. for $C_{14}H_{15}N_3O_4$: C, 58.1; H, 5.2; N, 14.5. Found: C, 57.8; H, 5.2; N, 14.3.

Reaction of **2b** with Sodium Methoxide/Methanol.

Compound **2b** (0.5 g., 1.25 mmoles) was refluxed for 70 hours with 1% sodium methoxide in methanol (30 ml.). The reaction mixture was evaporated, the residue washed with water and filtered. The crude product was recrystallized from isopropyl ether yielding the pure **8** as a white powder, m.p. 162-164°; yield 60%; nmr (deuteriochloroform): 2.10 (4H, m, CH_2NCH_2), 2.80 (2H, s, CH_2), 3.45 (4H, m, CH_2OCH_2), 3.70 (3H, s, Me), 6.50 (2H, m, NH_2, exchangeable), 7.21 (3H, m, aromatic).

Anal. Calcd. for $C_{15}H_{16}Cl_2N_2O_3$: C, 52.2; H, 5.25; N, 8.1. Found: C, 51.9; H, 5.1; N, 8.0.

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(8) The observed configuration is in agreement with the known stereospecificity of the cycloaddition of nitrile oxides to enamines (7) and corresponds to the probably more stable isomer in which the two bulkier residues are *trans*.

(9) ^{1}H-nmr spectra are not reported because they were of poor quality owing to solubility problems and allowed only qualitative conclusions.

(10) An example of 3,5-diaryl-4-methylene-5-trialkylhydrazino-4,5-dihydroisoxazole has been described (11).

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(12) The reactivity of compounds **4** with nucleophiles is described in Part 2 of this series (13).

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(16) A similar behaviour is known for some 5-amino-4-aminomethyl-4,5-dihydro-*v*-triazoles (1,17).

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(18) The intermediacy of **5a** and of its elimination product **4d** could be ruled out. The former did not suffer any significant change when reacted under similar conditions. Compound **4d** reacted easily with hydrochloric acid in aqueous ethanol yielding a mixture of products in which no **6** was present. As the main product 3-(4-bromophenyl)-4-ethoxymethylisoxazole was isolated.

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