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NEW TRICYCLIC PRODUCTS FROM THE REACTION OF 2,3-BUTANEDIONE AND ETHANOLAMINE

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Abstract: *Reinvestigation of the reaction of* 2,3-*butanedione with ethanolamine afforded the known cis*-4a,8a-*dimethyl*[1,4]-*oxazino*-[3,2-*b*][1,4]*oxazine as well as two new tricyclic products:* 12,13-*dimethyl*-2,7-*dioxa*-5,10-*diaza-tricycle*[4,4,4,$0^{1,6}$]*trans-tetradecan*-12-13-*diol, and N,N'*-[(4",5"-*dimethyl*) 1",2"-*phenylene*]-2,2'-*dimethylbisoxazolidine as established by X-ray analysis.*

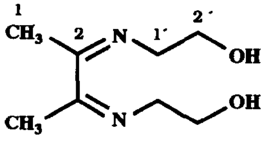
The condensation of α-diketones with aminoalcohols and aminophenols has been the subject of extensive investigations.[1,2] These reactions have been shown to proceed with remarkable regio- and stereoselectivity to provide a wide variety of products and are strongly influenced by the reaction conditions as well as the nature of reagents.

Our interest in the characterization of isomeric systems of the type bisoxazolidine/oxazino-oxazine by NMR methods[3] lead us to re-investigate the reaction of 2,3-butanedione and ethanolamine. In this particular case, it has been described that condensation of ethanolamine with 2,3-butanedione or benzil affords the corresponding α-diimines[4] (1) isolated as metal complexes. Another report describes the preparation of a bisoxazolidine from reaction of 2,3-butanedione with (S)-2-aminobutanol.[5] Studies of several N-substituted ethanolamines describe the formation of N,N'-bisoxazolidines, N-alkyl-2,3-epoxymorpholines and the isomerization products: N-alkyl-2-morpholone and the corresponding aminoacids,[1,6] while subsequent studies using the same N-substituted ethanolamines report the formation of completely different products: 2,3,5,6-dioxazino-dioxane and *cis*-oxazino-oxazine as established by X-ray diffraction analysis.[7]

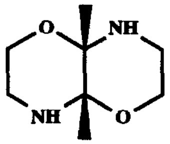
Curiously a parallel study describes the formation of *trans*[1,4]oxazino[3,2-b][1,4]oxazine by reaction of ethanolamine and 2,3-butanedione in a 2:1 molar ratio, based on the coupling constants of the peripheral methylene fragment; while use of a 1:1.5 molar ratio (excess butanedione) was claimed to afford 2,3,9,10-tetramethyl-2,3-epoxy-8-aza-1,4,5-trioxadecalin and later shown to give 5,6,8,9-tretramethyl-1-aza-4,7,10-trioxatricyclo-[4,3,0,$1^{5,9}$]decan-8-ol by X-Ray analysis.[9]

A recent structural study of the reaction of α-diketones with 2-aminoalcohols establishes that the 1:1 condensation of ethanolamine and 2,3-butanedione, 1-phenyl-1,2-propanedione or benzil leads to the corresponding 2-hydroxy-5,6-dihydro-2H-1,4-oxazines. The same reaction using an excess of 2,3-butanedione leads to the *cis*-oxazino-oxazine (2), as established by X-ray analysis, thus allowing to correct the previously assigned *trans* stereochemistry.[8]

The present study describes the formation of two new products: 12,13-dimethyl-2,7-dioxa-5,10-diazatricycle[4,4,4,$0^{1,6}$]*trans*-tetradecan-12,13-diol (3) and N,N′-[(4″,5″-dimethyl)1″,2″-phenylene]-2,2′-dimethyl-bisoxazolidine (4), obtained by reaction of ethanolamine with butanedione, whose structures were established by X-ray diffraction analysis.



1



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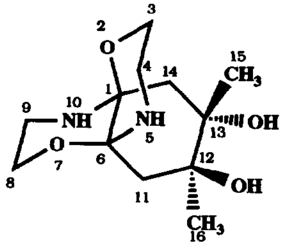

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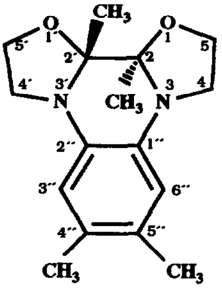


4

Results and Discussion

The 2:1 condensation of ethanolamine with 2,3-butanedione was carried out in benzene as described previously[2] using 5 h of reaction. This provided a benzene soluble fraction containing oxazino-oxazine 2, as established by comparison with the literature data[8], as well as an oily fraction consisting of diimine (1). The ^1H nmr spectrum of 1 showed a broad signal at 7.97 due to the hydroxylic proton, a triplet (J = 6 Hz) at 3.42, a quartet (J = 6) at 3.12 ppm, as well as a singlet (1.83 ppm) due to the methyl groups. Unambiguous assignment of the methylenic protons was attained by selective decoupling of the labile proton. This in turn allowed to correlate the signal at 3.42 ppm (H-1′) in the ^1H nmr spectrum with the corresponding carbon signal at 59.83 ppm using a two dimensional ^1H-^{13}C HETCOR experiment.

A different reaction outcome was observed when the condensation was carried out as above, the benzene soluble fraction was evaporated and the solid dissolved in MeOH/AcOEt or MeOH/Et_2O mixtures. This provided again 2 which was separated from the reaction mixture and a filtrate which was allowed to stand for a week to yield a new tricyclic product (3) obtained by condensation with a second equivalent of 2,3-butanedione. The same products were observed when the reaction was carried out without solvent.

The ^1H NMR spectrum of 3 showed an ABCD pattern for the methylene fragment with coupling constants and chemical shifts very similar to those of 2.[8] Evidence for the formation of a new ring was obtained from the AX system shown by CH_2-11 at 2.90 and 1.02 ppm ($J = 14.6$ Hz), as well as the disappearance of the methyl signal observed in 2. As expected, the ^{13}C NMR spectra of 2 and 3 also show similar chemical shifts, in the latter, however, the C-11 triplet (39.73 ppm) and C-12 singlet (74.16 ppm) were evident.

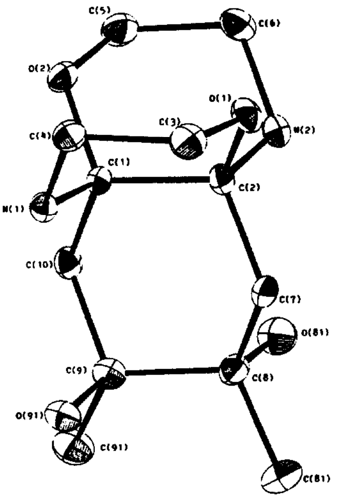
Moreover, the ABCD partern for compound 3 was subjected to a complete analysis using the LAOCOÖN-3 program, the coupling constants are summarized in the experimental part.

The X-ray crystal structure of 3 (Figure 1) shows three fused six-membered rings in a chair like conformation. In analogy to 2[2], tricycle 3 shows a stabilizing anomeric effect from the two nitrogen atoms whose nonbonding lone pairs are placed antiperiplanar to the C-O bonds. The O_1-C_2 (bridge) (1.450 (2) Å) and O_2-C_1 (1.448 (2) Å) bond distances are longer than the other O-C bonds distances (O_1-C_3, 1.431 (3) Å and O_2-C_5, 1.433 (3) Å) while the N-C (bridge) is shorter (N_1-C_1, 1.452 (3) Å and N_2-C_2, 1.457 (3) Å) than the other N-C bonds (N_1-C_4, 1.476 (3) Å and N_2-C_6, 1.474 (3) Å). Unit cell parameters and basic information about data collection and structure refinement of 3 and 4 are summarized in Table 1. Relevant bond lengths and angles are given in Tables 2 and 3.

On the other hand, if the reaction of 2,3-butanedione with ethanolamine is carried out as above, the benzene soluble fraction evaporated and dissolved in MeOH/ACOEt or MeOH/Et_2O mixtures without isolating 2, two different tricyclic products (3 and 4) may be obtained.

The ^1H nmr spectrum of 4 in C_6D_6 showed a singlet at 6.34 ppm due to the aromatic protons (H-3",6"), a complex pattern for the ethylenic fragment and two methyl singlets at 1.20 and 2.23 ppm due to the methyl groups at the fusion and at the aromatic ring, respectively. The ^{13}C nmr spectrum of 4 showed three distinct aromatic signals at 130.0 (C-1",2"), 125.8 (C-4",5") and 114.3 (C-3",6") which were assigned based on substituent effects.[10] The oxazolidine ring carbons were assigned using a two dimensional HETCOR experiment which showed that the two protons between 2.91-3.12 ppm can be correlated with the signal at 45.67 (CH_2N, C-4), while the lower field hydrogens give rise to the lower field triplet at 65.1 ppm (CH_2O, C-3) in the ^{13}C NMR spectrum, the methyl signals appearing at 17.6 ppm and 19.4 ppm for the methyl fusion and aromatic methyl protons, respectively.

The mechanism of formation of compounds 3 and 4 can be rationalized in terms of an imine-enamine equilibrium and is supported by isolation and characterization of diimine 1. Also reaction of oxazino-oxazine 2 with one mole of 2,3-butanedione afforded 3. Thus the double condensation of ethanolamine with butanedione via the 6-exo-trig mode of attack in 1 leads to the thermodynamically favored *cis*-oxazino-oxazine (2).[2] In turn, the enamine reacts stereoselectively with additional butanedione to provide *trans*-diol-3 and *trans*-bis-oxazolidine 4.



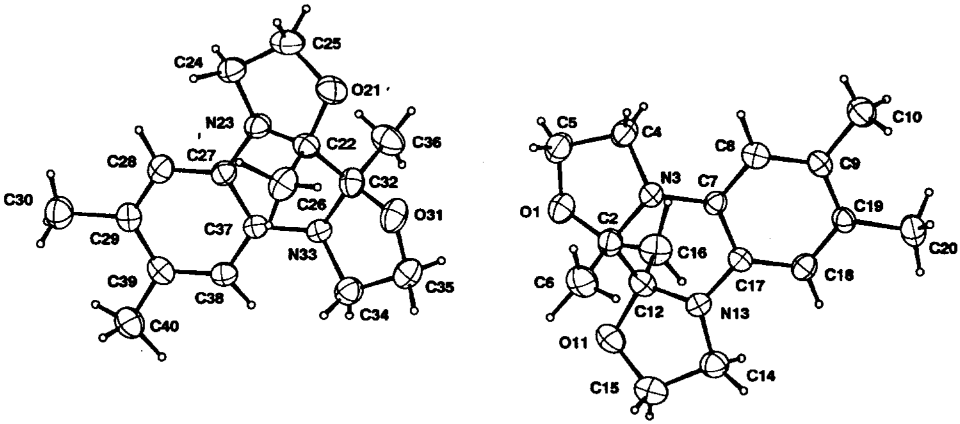


Figure 1.- Perspective view of the molecular structures of 3 and 4 Numbering system does not correspond to standard IUPAC nomenclature.

The X-ray crystal structure of 4 shows two fused oxazolidine rings with the aromatic ring fused to the two N-atoms. The C(2)-C(12) bond distance is shorter (1.518(7)) than the corresponding C(1)-C(2) bond distance in 3 (1.550(3) Å) and the analogous bisoxazolidine derived from ephedrine[3] (C(2)-C(2') bond distance 1.559(7)). The torsion angle for the C-6 and C-16 methyl groups at the bisoxazolidine ring fusion is 164°.

Conclusions

In agreement with previous reports, the condensation of ethanolamine and 2,3-butanedione was found to be strongly influenced by the nature of the solvent. Tricyclic products are indeed observed when the reaction is allowed to proceed for longer times. All reactions showed high stereoselectivity. Formation of cis-fused tricyclic product (3) can be attributed to anomeric effects and is indeed evident in the X-ray structure.

Table 1. Crystal data for compounds 3 and 4

	3	4
Formula	$C_{12}H_{22}N_2O_4$	$C_{16}H_{22}O_2N_2$
fw	258.32	274.36
system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a,Å	7.284(9)	7.737(3)
b,Å	9.182(5)	9.603(5)
c,Å	10.27(1)	19.713(5)
α,°	58.37(7)	89.43(3)
β,°	85.89(1)	95.26(3)
γ,°	78.68(1)	79.22(4)
V,$Å^3$	629(3)	1432(1)
Z	2	4
μ(MoKα),cm^{-1}	1.36	0.79
dcalc., g cm^{-3}	0.96	1.27
scan type	$\omega/2\theta$	$\omega/2\theta$
scan width,°	1.6+0.345tgθ	0.8+0.345tgθ
Diffractometer	Philips PW 1100	CAD4-Enraf-Nonius
no. of reflections collected	3019	5044
no. of unique reflections	2477	4882
merging R factor	0.05	0.03
no. of reflections with I>3σI)	1837	1611
R	0.060	0.042
Rw	0.066	0.040
no. of variables	231	362

Experimental

NMR spectra were recorded on a Jeol GSX-270 spectrometer in $CDCl_3$ or C_6D_6 using TMS as internal reference. Mass spectra were obtained with a Hewlett-Packard 5989-A spectrometer and infrared spectra were determined on a Nicolet MX-1FT spectrophotometer. Melting points were determined on a

GallenKamp MFB-595 apparatus and are uncorrected. The ABCD pattern for compound 3 was subjected to a complete analysis using the LAOCOÖN-3 program. Elemental analysis were performed by Oneida Research Services, Inc., New York.

Crystal data: A selected crystal was set up on an automatic diffractometer Unit cell dimensions with estimated standard deviations were obtained from least-squares refinements of the setting angles of 25 well contered reflections. Two standard reflections were monitored periodically; they showed no change during data collection. Crystallographic data and other pertinent information are summarized in Table 1. Corrections were made for Lorentz and polarization effects. Empirical absorption corrections (Difabs)[11] were applied.

Computations were performed by using CRYSTAL[12] adapted on a Micro Vax II. Atomic form factors for neutral C,N,O and H were taken from ref. 13.

Table 2. Interatomic distances (Å) for compounds 3 and 4

$C_{12}H_{22}N_2O_4$ (3)

N(1) - C(1)	1.452(3)	N(1) - C(4)	1.476(3)
N(2) - C(2)	1.457(3)	N(2) - C(6)	1.474(3)
O(1) - C(2)	1.450(2)	O(1) - C(3)	1.431(3)
O(2) - C(1)	1.448(2)	O(2) - C(5)	1.433(3)
O(81) - C(8)	1.439(3)	O(91) - C(9)	1.438(3)
C(1) - C(2)	1.550(3)	C(1) - C(10)	1.536(3)
C(2) - C(7)	1.534(3)	C(3) - C(4)	1.505(4)
C(5) - C(6)	1.505(4)	C(7) - C(8)	1.541(3)
C(8) - C(9)	1.560(3)	C(8) - C(81)	1.524(3)
C(9) - C(10)	1.532(3)	C(9) - C(91)	1.530(3)

$C_{16}H_{22}O_2N_2$ (4)

O(1) - C(2)	1.438(6)	O(1) - C(5)	1.434(7)
C(2) - N(3)	1.451(6)	C(2) - C(6)	1.548(7)
C(2) - C(12)	1.518(7)	N(3) - C(4)	1.448(7)
N(3) - C(7)	1.398(5)	C(4) - C(5)	1.498(7)
C(7) - C(8)	1.383(7)	C(7) - C(17)	1.398(6)
C(8) - C(9)	1.396(6)	C(9) - C(10)	1.510(7)
C(9) - C(19)	1.364(7)	O(11) - C(12)	1.416(6)
O(11) - C(15)	1.431(7)	C(12) - N(13)	1.458(6)
C(12) - C(16)	1.533(7)	N(13) - C(14)	1.442(6)
N(13) - C(17)	1.375(6)	C(14) - C(15)	1.510(7)
C(17) - C(18)	1.389(6)	C(18) - C(19)	1.380(7)
C(19) - C(20)	1.517(7)	O(21) - C(25)	1.414(7)
O(21) - C(22)	1.405(6)	C(22) - C(26)	1.521(7)
C(22) - N(23)	1.453(6)	N(23) - C(24)	1.448(6)
C(22) - C(32)	1.515(7)	C(24) - C(25)	1.506(8)
N(23) - C(27)	1.383(6)	C(27) - C(37)	1.380(6)
C(27) - C(28)	1.391(6)	C(29) - C(30)	1.507(7)
C(28) - C(29)	1.384(7)	O(31) - C(32)	1.413(6)
C(29) - C(39)	1.384(7)	C(32) - N(33)	1.455(6)
O(31) - C(35)	1.418(6)	N(33) - C(34)	1.460(7)
C(32) - C(36)	1.534(7)	C(34) - C(35)	1.495(7)
N(33) - C(37)	1.402(6)	C(38) - C(39)	1.399(6)
C(37) - C(38)	1.375(7)	C(39) - C(40)	1.488(7)

Table 3. Bond angles (deg) for compounds 3 and 4

$C_{12}H_{22}N_2O_4$ (3)			
C(4) - N(1) - C(1)	113.4(2)	C(6) - N(2) - C(2)	113.4(2)
C(3) - O(1) - C(2)	114.9(2)	C(5) - O(2) - C(1)	115.3(2)
O(2) - C(1) - N(1)	106.8(2)	C(2) - C(1) - N(1)	109.2(2)
C(2) - C(1) - O(2)	111.1(2)	C(10) - C(1) - N(1)	107.8(2)
C(10) - C(1) - O(2)	109.9(2)	C(10) - C(1) - C(2)	111.8(2)
O(1) - C(2) - N(2)	106.4(2)	C(1) - C(2) - N(2)	109.5(2)
C(1) - C(2) - O(1)	110.8(2)	C(7) - C(2) - N(2)	108.0(2)
C(7) - C(2) - O(1)	110.4(2)	C(7) - C(2) - C(1)	111.6(2)
C(4) - C(3) - O(1)	110.6(2)	C(3) - C(4) - N(1)	108.4(2)
C(6) - C(5) - O(2)	110.4(2)	C(5) - C(6) - N(2)	109.7(2)
C(8) - C(7) - C(2)	115.0(2)	C(7) - C(8) - O(81)	110.6(2)
C(9) - C(8) - O(81)	108.5(2)	C(9) - C(8) - C(7)	109.0(2)
C(81) - C(8) - O(81)	106.7(2)	C(81) - C(8) - C(7)	109.3(2)
C(81) - C(8) - C(9)	112.7(2)	C(8) - C(9) - O(91)	110.4(2)
C(10) - C(9) - O(91)	110.7(2)	C(10) - C(9) - C(8)	109.0(2)
C(91) - C(9) - O(91)	105.6(2)	C(91) - C(9) - C(8)	111.8(2)
C(91) - C(9) - C(10)	109.3(2)	C(9) - C(10) - C(1)	114.6(2)
$C_{16}H_{22}O_2N_2$ (4)			
C(2) - O(1) - C(5)	106.8(4)	O(1) - C(2) - N(3)	104.3(4)
O(1) - C(2) - C(6)	109.4(4)	N(3) - C(2) - C(6)	112.5(5)
O(1) - C(2) - C(12)	109.1(4)	N(3) - C(2) - C(12)	110.0(4)
C(6) - C(2) - C(12)	111.4(5)	C(2) - N(3) - C(4)	110.3(4)
C(2) - N(3) - C(7)	121.4(4)	C(4) - N(3) - C(7)	120.8(4)
N(3) - C(4) - C(5)	103.0(5)	O(1) - C(5) - C(4)	104.5(4)
N(3) - C(7) - C(8)	121.6(5)	N(3) - C(7) - C(17)	119.5(4)
C(8) - C(7) - C(17)	118.9(4)	C(7) - C(8) - C(9)	121.5(5)
C(8) - C(9) - C(10)	119.4(5)	C(8) - C(9) - C(19)	119.3(5)
C(10) - C(9) - C(19)	121.3(5)	C(12) - O(11) - C(15)	110.0(4)
C(2) - C(12) - O(11)	112.6(4)	C(2) - C(12) - N(13)	105.4(4)
O(11) - C(12) - N(13)	103.4(4)	C(2) - C(12) - C(16)	112.7(5)
O(11) - C(12) - C(16)	109.3(5)	N(13) - C(12) - C(16)	113.1(4)
C(12) - N(13) - C(14)	107.8(4)	C(12) - N(13) - C(17)	116.1(4)
C(14) - N(13) - C(17)	125.3(4)	N(13) - C(14) - C(15)	101.4(4)
O(11) - C(15) - C(14)	106.3(5)	C(7) - C(17) - N(13)	116.8(4)
C(7) - C(17) - C(18)	118.8(4)	N(13) - C(17) - C(18)	124.4(5)
C(17) - C(18) - C(19)	121.7(5)	C(9) - C(19) - C(18)	119.9(5)
C(9) - C(19) - C(20)	121.3(5)	C(18) - C(19) - C(20)	118.9(5)
C(22) - O(21) - C(25)	109.2(4)	O(21) - C(22) - N(23)	104.0(4)
O(21) - C(22) - C(26)	108.8(4)	N(23) - C(22) - C(26)	113.5(4)
O(21) - C(22) - C(32)	113.0(4)	N(23) - C(22) - C(32)	105.3(4)
C(26) - C(22) - C(32)	111.9(5)	C(22) - N(23) - C(24)	107.0(4)
C(22) - N(23) - C(27)	116.3(4)	C(24) - N(23) - C(27)	124.9(4)
N(23) - C(24) - C(25)	101.2(4)	O(21) - C(25) - C(24)	107.5(4)
N(23) - C(27) - C(28)	123.4(5)	N(23) - C(27) - C(37)	117.0(4)
C(28) - C(27) - C(37)	119.6(5)	C(27) - C(28) - C(29)	121.3(5)
C(28) - C(29) - C(30)	119.8(5)	C(28) - C(29) - C(39)	119.6(5)
C(30) - C(29) - C(39)	120.5(5)	C(32) - O(31) - C(35)	108.0(4)
C(22) - C(32) - O(31)	110.1(4)	C(22) - C(32) - N(33)	110.5(4)
O(31) - C(32) - N(33)	104.7(4)	C(22) - C(32) - C(36)	112.0(5)
O(31) - C(32) - C(36)	109.1(4)	N(33) - C(32) - C(36)	110.1(4)
C(32) - N(33) - C(34)	109.6(4)	C(32) - N(33) - C(37)	121.4(4)
C(34) - N(33) - C(37)	120.8(4)	N(33) - C(34) - C(35)	102.5(5)
O(31) - C(35) - C(34)	105.0(4)	C(27) - C(37) - N(33)	119.5(4)
C(27) - C(37) - C(38)	118.9(5)	N(33) - C(37) - C(38)	121.6(5)
C(37) - C(38) - C(39)	122.3(5)	C(29) - C(39) - C(38)	118.4(5)
C(29) - C(39) - C(40)	122.3(5)	C(38) - C(39) - C(40)	119.3(5)

The structure was solved by direct method using the SHELXS86 program.[14] Hydrogen atoms were found on difference electron density maps. Their atomic coordinates were refined with an overall isotropic temperature factor. Anisotropic temperature factors were introduced for all non-hydrogen atoms. Least-squares refinements with approximation in three blocks to the normal matrix were carried out by minimizing the function $\Sigma w(|F_o|-F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. Unit weight was used. Models reached convergence with $R = \Sigma(||F_o|-|F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ having values listed in Table 1. Criteria for a satisfactory complete analysis were the ratios of rms shift to standard deviation being less than 0.1 and no significant features in final difference map.

Supplementary Material available: Tables of atomic coordinates, anisotropic temperature factors, hydrogen coordinates, distances and angles involving H atoms and observed and calculated structure factors. Ordering information is given on any current masthead page.

2,3-Butanedione and ethanolamine were commercially available products (Aldrich).

Condensation of 3.6 g (0.04 mole) of butanedione with 5 g (0.08 mole) of ethanolamine was carried out in benzene using 5 h of reaction at room temperature, as described in ref. 2. This yielded a benzene soluble fraction which was filtered over $MgSO_4$, concentrated and the solid washed with AcOEt to provide 2.02 g (33%) of ***cis*-4a,8a-dimethyl[1,4]oxazino[3,2-b][1,4]oxazine** (2), mp 107-110°C (Lit[8] 106-108°C) and an oily fraction which was also washed with ACOEt to provide 1.28 g (13.2%) of **N,N'-Bis-(2-hydroxyethyl)-2,3-butanediimine** (1). ^1H NMR (270 MHz, DMSO-d_6) δ: 7.97 (1H, b, OH), 3.42 (2H, t, J = 6 Hz, H-1'), 3.12 (2H, q, J = 6, H-2'), 1.83 (3H, s, CH_3); ^{13}C NMR (67.8 MHz, DMSO-d_6): 170.00 (s, C = N), 59.83 (t, C-1'), 41.55 (t, C-2'), 22.46 (q, CH_3); IR (film) ν_{max} 3332, 1652, 1556, 1436, 1376, 1298, 1067 cm^{-1}.

12,13-Dimethyl-2,7-dioxa-5,10-diazatricycle-[4,4,4,$0^{1,6}$]*trans*-Tetradecan-12,13-diol (3). Tricycle 3 was obtained when the benzene soluble fraction was concentrated, solid 2 removed by filtration and the filtrate dissolved in MeOH/AcOEt (1:1 v/v) and allowed to stand for a week (1.8 g, 17%) or in MeOH/Et_2O (1:9 v/v) overnight (2.3 g, 22%) mp 152-154°C. The same product (3) was obtained when oxazino-oxazine (2) was dissolved in MeOH/AcOEt, butanedione was added and the solution was allowed to stand for a week. ^1H nmr ($CDCl_3$, 270 MHz) 3.96(1H, J_{gem}= 10.9, J_{axax}= 11.8, J_{axeq}= 2.8 Hz, H-3ax), 3.76(1H, J_{gem}= 10.9, J_{eqax}= 3.8Hz, J_{eqeq}= 0.8

Hz, H-3eq), 3.47(1H, J_{gem}= 11.1, J_{axax}= 11.8, J_{axeq}= 3.8 Hz, H-4ax), 2.50 (1H, J_{gem}= 11.1, J_{eqax}= 2.8, J_{eqeq}= 0.8 Hz, H-4eq), 2.90 and 1.02(1H each, J = 14.6, CH_2-11), 1.19(3H, s, 12-CH_3) ; ^{13}C nmr ($CDCl_3$, 67.8 MHz) 82.55 (s, C-1), 74.16(s, C-12), 62.06(t, C-3), 39.73 (t, C-11), 38.14(t, C-4), 22.20(q, 12-CH_3); IR ν_{max} (KBr) ν_{max}: 3350 (OH) 3291, 3257(N-H), 2969, 1434, 1129, 1097, 1083, 987 and 831; MS m/z (%) 258(M^+, 0.1), 240(M^+-H_2O, 0.1) 199 (5), 117(10), 44(54), 43 (100),42 (26) and 41 (23). (Anal. Calcd. for $C_{12}H_{22}N_2O_4$: C, 55.80; H, 8.53; N, 10.80. found: C, 55.43; H, 8.28; N, 10.90).

N,N'[(4",5"-Dimethyl)1",2"-phenylene]-2,2'-dimethyl-bisoxazolidine (4). Reaction of 3.6 g (0.04 mol) of butanedione with 5 gr (0.08 mol) ethanolamine was carried out as described above. The benzene soluble fraction was concentrated dissolved in MeOH/AcOEt (1:1 v/v) and allowed to stand for a week without isolating 2. The solid was washed with MeOH to provide (3.06 g, 2.9 %) of 3 and the filtered solution was allowed to stand to provide (1.05 g, 9.3%) of 4 which was washed with EtOH, mp 126-128°C. ^1H NMR (270 MHz, C_6D_6): 6.34(1H, s, H-3"), 3.82-3.68(2H, m, H-5), 3.12-2.91(2H, m, H-4), 2.23(3H, s, 4"-CH_3), 1.20(3H, s, 2-CH_3); ^{13}C NMR (67.8 MHz, C_6D_6): 130.05(s, C-1"), 125.77(s, C-4"), 114.27(d, C-3"), 93.00(s, C-2), 65.01(t, C-5), 45.67(t, C-4), 19.44(q, 4"-CH_3), 17.63(q, 2-CH_3); IR ν_{max} (KBr): 3854, 3744, 3676, 3628, 3020 (=C-H), 1653, 1525, 1473, 1358 and 1314; MS *m/z* (%): 275(M^+ + 1, 15), 274(M^+, 82), 273(26),232(16), 231 (100), 216(20), 215(33), 189(27), 188(21), 187(11), 174(49), 173 (16), 161(17), 160(16), 159(15), 147(27), 146(25), 145(10) 91(15), 77(15), 43(96), 39(9), 27(19) and 15(12). (Anal. Calcd. for $C_{16}H_{22}O_2N_2$: C, 70.10; H, 8.03; N, 10.20. Found: C, 69.92; H, 7.86; N, 10.22).

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