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1-OXA-3-AZAPENTALEN-2-ONES AS PRECURSORS OF *cis*-2-AMINO ALCOHOLS: SYNTHESIS FROM PROPARGYL ALCOHOLS, CO_2, AND AMINES USING AN INTRAMOLECULAR AMIDOALKYLATION REACTION OF OXAZOLIDIN-2-ONES.

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The reaction of 5-methyl-5-(4-methyl-3-pentenyl)-4-methylene-1,3-dioxolan-2-one with primary amines gives the corresponding 4-hydroxy-4-methyloxazolidin-2-ones. These undergo an intramolecular amidoalkylation reaction to form 1-oxa-3-azapentalen-2-ones which are potential precursors of cyclopentanyl cis-2-amino alcohols.

Keywords: 2-amino alcohols, 4-hydroxyoxazolidin-2-ones, 4-methylene-1,3-dioxolan-2-ones, 1-oxa-3-azapentalen-2-ones, intramolecular amidoalkylation, X-ray structural analysis, stereoselectivity.

Several chiral 2-amino alcohols are of significant interest as components for the preparation of catalysts for Diels–Alder [1], Michael [2], and enantioselective reduction [3] type asymmetric reactions. In addition, 2-amino alcohols show a broad spectrum of biological activity.

In this work we propose a simple route to the precursors of cyclopentanyl *cis*-2-amino alcohols *via* the reaction of the dioxolanone **1a** [4] with primary amines **2** which leads to the intermediate oxazolidinones **3** [5]. An intramolecular amidoalkylation of the oxazolidinones **3** in HCOOH then permits the preparation of the azapentalenones **4** and **5** with *cis*-orientated methyl groups at the ring junctions. Compounds **4** and **5** are under consideration as potential precursors of the *cis*-2-amino alcohols mentioned.

In addition to the indicated method for the synthesis of the oxazolidinones **3** [5] there also exist other routes for the preparation of these substances. Despite the formation of side products, modest yields, and the complexity of the procedure, several oxazolidinones **3** are more readily synthesized *via* addition of organometallic compounds to oxazolidin-2,4-diones [6, 7]. A method has also been proposed for 4-methoxyoxazolidin-2-ones (materials related to the oxazolidinones **3**) *via* the use of Sn- and Se-organic compounds which give good yields and are stereospecific [8]. The amidoalkylation of 4-hydroxythiazolidin-2-ones is covered by the review [8] but the amidoalkylation of the oxazolidinones **3** has seen little work other than the articles referred to [6, 7] and our paper [10].

The reaction of the amines **2** with dioxolanones **1** occurs over 12-144 hours at room temperature to give 38-100% yields of the oxazolidinones **3a-g,i** (**3h** was prepared at 110°C).

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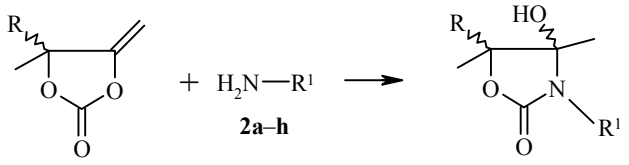
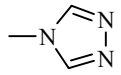
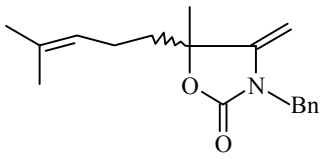


1a,**b** **3a–i**

1 a R = Dhl, **b** R = Me, **2 a** R^1 = Bn, **b** R^1 = 2-$PyCH_2$, **c** R^1 = $NCCH_2CH_2$, **d** R^1 = CH_2=$CHCH_2$, **e** R^1 = $HOCH_2CH_2$, **f** R^1 = Me_2N, **g** R^1 = Tzl, **h** R^1 = 3-$PyCH_2$; **3 a–c**, **e–i** R = Dhl, **d** R = Me; **a** R^1 = Bn, **b** R^1 = 2-$PyCH_2$, **c** R^1 = $NCCH_2CH_2$, **d**, **e**, R^1 = CH_2=$CHCH_2$, **f** R^1 = $HOCH_2CH_2$, **g** R^1 = Me_2N, **h** R^1 = Tzl, **i** R^1 = 3-$PyCH_2$

Dhl = Me_2C=$CHCH_2CH_2$, Tzl = 

Catalysis by a Lewis base (in our case NEt_3) is needed for the less active N,N-dimethylhydrazine (**2f**) and the amines **2c** and **2g**. The structure of the oxazolidinones **3** was confirmed by their ^{1}H NMR spectra in which signals for both the 4-OH and the 4-Me groups are present [5]. The benzyl-type methylene protons in the oxazolidinones **3a,b,i** are revealed as two doublets with a small spin-spin coupling due to the presence of an asymmetric center at position 4 of the oxazolidinone ring. If there are two asymmetric centers in the molecule (two epimers) the interpretation of the ^{1}H NMR spectra becomes more difficult due to doubling of the signals. Such a mixture of epimers appears on TLC as two spots. Their melting points are unclear (in addition, several oxazolidinones of the type **3** are unstable and can lose water not only upon heating but even at room temperature [5]). The mixture of epimers of **3a** was chromatographically separated into the two epimers and their ^{1}H NMR spectra and melting points found to be different. Over one week in $CDCl_3$ solution containing traces of DCl both pairs are converted to the same product which was characterized by ^{1}H NMR spectroscopy as 3-benzyl-5-methyl-5-(4-methyl-3-pentenyl)-4-methyleneoxazolidin-2-one.



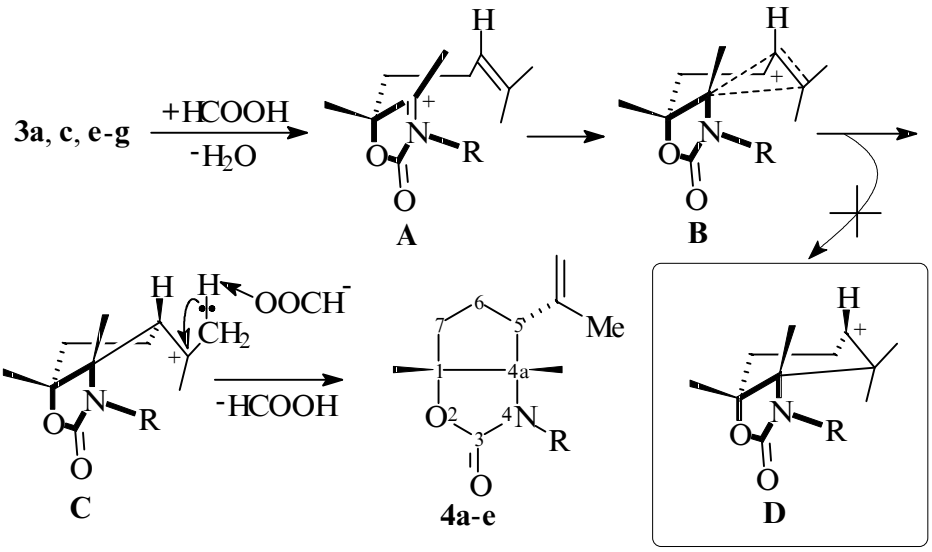
We have found that the amidoalkylation of the oxazolidinones **3** occurs at room temperature over 48-168 hours to give 26-96% yields of the azapentalenones **4a-e**.

In the case of compounds **3d,e** the allyl groups in position 3 of the oxazolidinone ring do not undergo attack at the acyliminium center since this would demand a geometrically unfavored 5-*endo*-trig transition state [11]. For the azapentalenone **4d** an acylation of the β-hydroxyethyl group by the formyl residue is observed (Scheme 1)

We have not attempted to establish the absolute configuration of the azapentalenones **4a-e** but, based on theoretical grounds [7, 11] and X-ray structural data for compound **5'** (see later) we propose that the azapentalenones **4a-e** must have the indicated stereochemistry*. The methyl groups on the vicinal atoms of the bicyclic fragment are *cis*-orientated and the propenyl group at position 5 is *endo*-orientated.

* Compounds **4a-e** are racemates since the starting dioxolanone **1a** is also a racemate and so the azapentalenones **5'** and **5''** are also racemates and the material **4f'/4f''** is a mixture of epimers (see later).

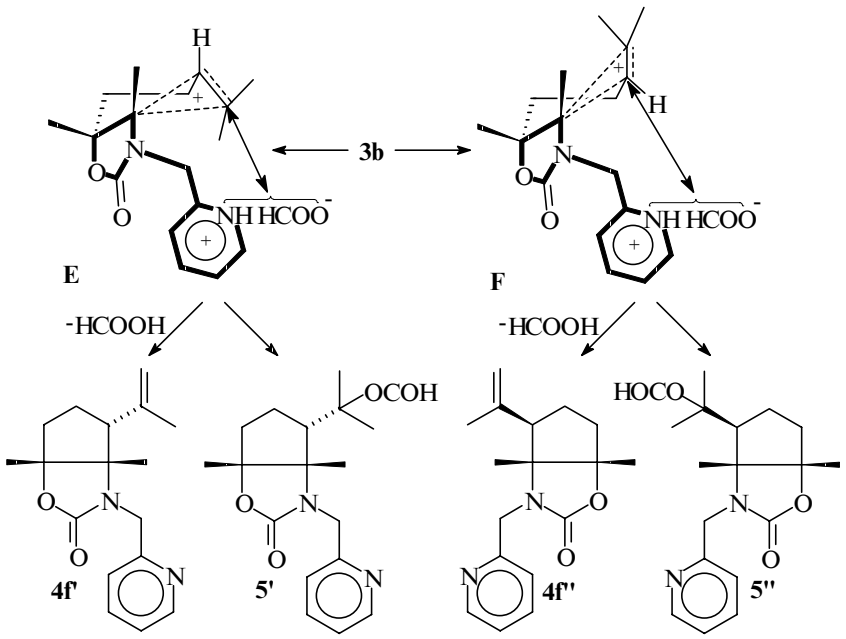
Scheme 1



4 a R = $PhCH_2$, **b** R = $NCCH_2CH_2$, **c** R = CH_2=$CHCH_2$, **d** R = $HCOOCH_2CH_2$, **e** R = Me_2N

The reaction takes place by a standard mechanism. The acyliminium center reacts with the double bond in the molecule **A** in such a way as to ensure maximum overlap of the molecular orbitals and minimization of the energy in the newly formed ring upon transition to the three centered ion **B**. The molecule **B** is then converted to the tertiary carbocation **C** having a five-membered ring. Although, from an energetic point of view, the five-membered ring is comparable with a six-membered the latter is not formed because it would demand the generation of the less stable secondary carbocation **D**. The stabilization of the tertiary carbocation **C** can occur by two routes: elimination of a proton or the addition of the $HCOO^-$ anion. Formation of the unsaturated azapentalenones **4a-e** suggests that the rate of proton loss is much higher than the rate of addition of the counterion. In all cases a loss of a proton from one of the methyl groups of the isopropyl carbocation **C** is observed and not a proton of the cyclopentane ring. However, both the elimination of the proton and the addition of the formate anion is observed if, in position 3 of the oxazolidinone ring, there is located a substituent which can be protonated (with the exception of compound **4e** where only the proton elimination occurs).

Hence the starting oxazolidinone **3b** yields the four products **4f'/4f''**, **5'**, and **5''**. We were able to separate compounds **5'** and **5''** chromatographically but compounds **4f'/4f''** could only be isolated as a mixture (according to ^{1}H NMR the ration of **4'** to **4''** was ~ 1:1). The ^{1}H NMR data for the products of amidoalkylation of oxazolidinones **3h,i** suggest that products analogous to **4f'/4f''**, **5'**, and **5''** are present in the reaction mixtures. Evidently the formation of the fomyloxy derivatives **5** is due to the possibility of coordination of the formate anion with the protonated pyridine ring. The carbocations **E** and **F** (analogs of **C**) can be stabilized both by the loss of a proton and by the addition of the coordinated formate anion. Evidently the rates of both processes are similar since the yields of **4f'**+**4f''** and **5'**+**5''** are comparable. The formation of the stereoisomeric products **4f'/5'** and **4f''/5f''** are controlled by two opposing factors: the tendency towards maximum overlap of the interacting molecular orbitals of the double bond and the acyliminium center on the one hand and the repulsion of the two positively charged acyliminium ion and pyridinium ring centers on the other. Since the yields of **4f'**+**5'** and **4f''**+**5''** are almost identical both factors are also most likely to be comparable in the magnitude of their effects.



The configuration of the ester **5'** was determined by an X-ray structural method (Fig. 1). As expected, the methyl groups on the vicinal atoms of the bicyclic fragment are *cis*-orientated and the 5-C(Me)$_2$–O–CO–H *endo*-orientated. The torsional angles $C_{(22)}$–$C_{(12)}$–$C_{(11)}$–$C_{(21)}$ and $C_{(13)}$–$C_{(14)}$–$C_{(15)}$–$C_{(16)}$ are 25.8(4) and -165.6(3)° respectively. The oxazolidinone ring has a twist conformation with a deviation of atoms $C_{(11)}$ and $C_{(12)}$ of 0.218 Å and -0.186 Å respectively. The cyclopentane ring is a distorted envelope with a deviation of the $C_{(13)}$ atom of 0.559 Å. The angle between the two annelated rings is 76°. Due to the weak C–H···O interaction at $C_{(18)}$–$H_{(18)}$···$O_{(20)}$ (-*x*, 1/2 + *y*, 1/2 - *z*) [$C_{(18)}$···$O_{(20)}$ 3.234(4), $C_{(18)}$–$H_{(18)}$ 0.990(5), $H_{(18)}$···$O_{(20)}$ 2.430(5) Å, angle $C_{(18)}$–$H_{(18)}$···$O_{(20)}$ 138(3)°] the molecules form a spiral around the crystallographic *b* axis (Fig. 2).

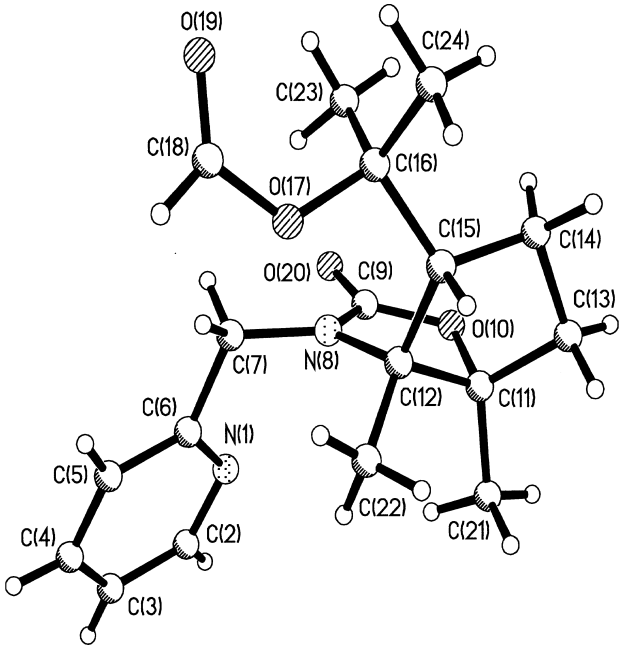


Fig. 1. Azapentalenone **5'**.

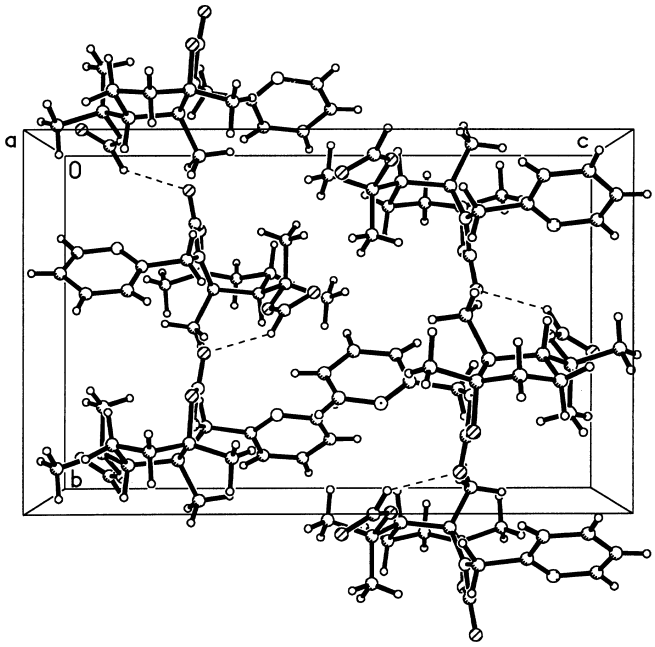


Fig. 2. Crystal lattice for the azapentalenone **5'**.

Almost all of the remaining bond lengths *d* (Table 1) and angles ω (Tables 2 and 3) have expected values [12]. Table 4 shows the atomic coordinates ($\times 10^4$) and isotropic thermal parameters (equivalent for non hydrogen atoms).

The azapentalenone stereoisomers **5'** and **5''** show different chemical shifts for the formyl and 3-CH_2–2'–Py group protons in their ^{1}H NMR spectra (in addition, compound **5'** is a solid material and **5''** an oil). On the basis of the spectroscopic data the compound **5''** can be assigned the structure with an *exo*-orientated 5-$C(Me)_2$–O–CO–H substituent.

Dilution of the reaction mixture leads to an increased yield of the target products in agreement with literature data. The yield of **4a** increases from 54 to 65% when the initial concentration of the oxazolidinone **3a** is lowered from 0.111 to 0.055 mmol/ml. Mass spectroscopic data indicates that the side products isolated have a doubled molecular weight for **3a** minus two molecules of water. These are evidently dimers, the formation of which has been discussed in [9].

TABLE 1. Bond Lengths in the Azapentalenone Molecule **5'**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
O(10)–C(9)	1.340(4)	C(11)–C(21)	1.503(5)	C(13)–C(14)	1.512(5)
O(10)–C(11)	1.482(4)	O(20)–C(9)	1.211(4)	C(14)–C(15)	1.531(5)
O(17)–C(18)	1.326(5)	N(1)–C(6)	1.327(4)	N(8)–C(12)	1.470(4)
O(17)–C(16)	1.468(4)	N(1)–C(2)	1.339(4)	C(2)–C(3)	1.355(6)
O(19)–C(18)	1.185(5)	N(8)–C(9)	1.339(4)	C(3)–C(4)	1.355(6)
C(4)–C(5)	1.366(6)	N(8)–C(7)	1.436(4)	C(15)–C(16)	1.550(5)
C(5)–C(6)	1.381(5)	C(11)–C(12)	1.559(4)	C(16)–C(23)	1.504(5)
C(6)–C(7)	1.516(5)	C(12)–C(22)	1.504(4)	C(16)–C(24)	1.531(5)
C(11)–C(13)	1.497(5)	C(12)–C(15)	1.578(4)		

TABLE 2. Angles in the Azapentalenone Molecule **5'**

Angle	ω, deg.	Angle	ω, deg.
C(9)–O(10)–C(11)	110.1(2)	C(14)–C(15)–C(16)	113.9(3)
C(18)–O(17)–C(16)	121.6(3)	N(1)–C(6)–C(7)	117.9(3)
C(6)–N(1)–C(2)	116.4(3)	C(5)–C(6)–C(7)	120.2(3)
C(9)–N(8)–C(7)	121.6(3)	N(8)–C(7)–C(6)	114.9(3)
C(9)–N(8)–C(12)	112.2(2)	O(20)–C(9)–N(8)	127.6(3)
C(7)–N(8)–C(12)	126.0(3)	O(20)–C(9)–O(10)	122.3(3)
N(1)–C(2)–C(3)	125.0(4)	N(8)–C(9)–O(10)	110.0(3)
C(4)–C(3)–C(2)	117.8(4)	O(10)–C(11)–C(13)	106.7(3)
C(3)–C(4)–C(5)	119.2(4)	O(10)–C(11)–C(21)	107.4(3)
C(4)–C(5)–C(6)	119.5(4)	C(13)–C(11)–C(21)	116.6(3)
N(1)–C(6)–C(5)	121.9(3)	O(10)–C(11)–C(12)	101.9(2)
C(13)–C(11)–C(12)	106.5(3)	C(14)–C(15)–C(12)	106.3(3)
C(21)–C(11)–C(12)	116.4(3)	C(16)–C(15)–C(12)	120.7(3)
N(8)–C(12)–C(22)	111.8(3)	O(17)–C(16)–C(23)	111.7(3)
N(8)–C(12)–C(11)	100.0(2)	O(17)–C(16)–C(24)	109.9(3)
C(22)–C(12)–C(11)	114.3(3)	C(23)–C(16)–C(24)	110.4(3)
N(8)–C(12)–C(15)	115.1(2)	O(17)–C(16)–C(15)	102.0(2)
C(22)–C(12)–C(15)	111.5(3)	C(23)–C(16)–C(15)	113.7(3)
C(11)–C(12)–C(15)	103.4(2)	C(24)–C(16)–C(15)	108.7(3)
C(11)–C(13)–C(14)	104.8(3)	O(19)–C(18)–O(17)	126.4(4)
C(13)–C(14)–C(15)	103.3(3)		

TABLE 3. Basic Torsional Angles (τ) in the Azapentalenone Molecule **5'**

Angle	τ, deg.	Angle	τ, deg.
C(9)–N(8)–C(7)–C(6)	80.4(4)	N(8)–C(12)–C(15)–C(16)	33.1(4)
N(1)–C(6)–C(7)–N(8)	-35.4(5)	C(9)–N(8)–C(12)–C(11)	-19.7(3)
C(7)–N(8)–C(9)–O(20)	15.6(5)	C(7)–N(8)–C(12)–C(11)	155.7(3)
C(7)–N(8)–C(9)–O(10)	-167.7(3)	C(9)–N(8)–C(12)–C(15)	90.4(3)
C(12)–N(8)–C(9)–O(10)	7.8(3)	C(7)–N(8)–C(12)–C(15)	-94.3(3)
C(11)–O(10)–C(9)–N(8)	9.0(4)	O(10)–C(11)–C(12)–N(8)	22.6(3)
C(9)–O(10)–C(11)–C(13)	-131.9(3)	C(13)–C(11)–C(12)–N(8)	134.2(3)
C(9)–O(10)–C(11)–C(12)	-20.5(3)	C(21)–C(11)–C(12)–C(22)	25.8(4)
C(7)–N(8)–C(12)–C(22)	34.3(4)	O(10)–C(11)–C(12)–C(15)	-96.4(3)
C(13)–C(11)–C(12)–C(15)	15.2(3)	C(11)–C(12)–C(15)–C(16)	141.1(3)
O(10)–C(11)–C(13)–C(14)	73.5(4)	C(18)–O(17)–C(16)–C(23)	-60.4(4)
C(12)–C(11)–C(13)–C(14)	-34.8(4)	C(18)–O(17)–C(16)–C(24)	62.5(5)
C(11)–C(13)–C(14)–C(15)	40.3(4)	C(18)–O(17)–C(16)–C(15)	177.8(3)
C(13)–C(14)–C(15)–C(16)	-165.6(3)	C(12)–C(15)–C(16)–O(17)	53.6(4)
C(13)–C(14)–C(15)–C(12)	-30.3(4)	C(12)–C(15)–C(16)–C(23)	-66.8(4)
N(8)–C(12)–C(15)–C(14)	-98.5(3)	C(12)–C(15)–C(16)–C(24)	169.7(3)
C(11)–C(12)–C(15)–C(14)	9.5(3)	C(16)–O(17)–C(18)–O(19)	-1.1(6)

Hence the azapentalenones **4** and **5** obtained have the indicated stereochemistry. All the stages of the synthesis (dioxolanone **1** to oxazolidinone **3** to azapentalenones **4** and **5**) are characterized by good yields, mild conditions, and ready separation of products (moreover, the oxazolidinones **3** can be used without purification). Hydrolysis of the azapentalenones **4** is the theme of subsequent publications; an example of the hydrolysis of related compounds can be found in our work [10].

TABLE 4. Coordinates ($\times 10^4$) and Isotropic (Equivalent for Non-hydrogen Atoms) Atomic Thermal Parameters in the Azapentalenone **5'**

Atom	*x*	*y*	*z*	*U*
O(10)	087(2)	7099(2)	2561(1)	58(1)
O(17)	696(3)	9595(2)	1138(1)	53(1)
O(19)	-968(4)	9128(3)	250(2)	96(1)
O(20)	2144(3)	5921(2)	2720(2)	68(1)
N(1)	964(3)	7749(3)	4058(2)	61(1)
N(8)	1975(2)	7990(2)	2518(1)	40(1)
C(2)	594(5)	7885(4)	4799(2)	70(1)
C(3)	-545(5)	8544(4)	5054(3)	68(1)
C(4)	-1334(5)	9160(4)	4525(3)	70(1)
C(5)	-990(4)	9056(4)	3762(3)	60(1)
C(6)	148(3)	8322(3)	3544(2)	46(1)
C(7)	477(3)	8122(4)	2697(2)	51(1)
C(9)	2666(3)	6926(3)	2621(2)	48(1)
C(11)	4414(3)	8427(3)	2525(2)	47(1)
C(12)	2944(3)	8976(3)	2267(1)	38(1)
C(13)	5428(4)	8603(4)	1864(2)	56(1)
C(14)	4509(4)	8450(4)	1152(2)	56(1)
C(15)	3115(4)	9111(3)	1366(2)	42(1)
C(16)	1842(4)	8823(3)	818(2)	48(1)
C(18)	-594(5)	9651(4)	815(2)	64(1)
C(21)	4949(5)	8805(5)	3307(2)	66(1)
C(22)	2575(5)	10180(3)	2639(2)	51(1)
C(23)	1422(6)	7492(4)	808(2)	60(1)
C(24)	2228(6)	9258(5)	5(2)	77(1)
H(2)	1039(40)	7451(35)	5141(22)	57(11)
H(3)	-741(53)	8537(42)	5572(30)	98(15)
H(4)	-2118(52)	9669(41)	4641(26)	88(14)
H(5)	-1459(42)	9381(32)	3376(22)	55(11)
H(71)	29(44)	7368(45)	2566(25)	87(14)
H(72)	-50(37)	8780(34)	2404(21)	58(10)
H(131)	6195(44)	8083(37)	1879(21)	66(11)
H(132)	5759(39)	9471(36)	1922(20)	57(10)
H(141)	5065(40)	8836(38)	705(25)	74(12)
H(142)	4457(48)	7536(47)	1068(23)	92(14)
H(15)	3381(36)	10013(32)	1300(17)	47(9)
H(18)	-1131(49)	10351(42)	1039(24)	85(13)
H(211)	5779(45)	8393(33)	3383(21)	60(11)
H(212)	5199(46)	9752(47)	3277(26)	85(14)
H(213)	4215(42)	8630(32)	3641(20)	47(9)
H(221)	3319(39)	10759(31)	2531(19)	55(10)
H(222)	1754(43)	10467(31)	2396(21)	68(10)
H(223)	2508(43)	10043(40)	3201(28)	78(12)
H(231)	728(41)	7371(31)	460(21)	53(10)
H(232)	2076(54)	6991(50)	607(29)	104(17)
H(233)	923(44)	7253(34)	1274(22)	63(11)
H(241)	3003(68)	8657(57)	-122(34)	134(22)
H(242)	1447(43)	9093(31)	-345(22)	58(10)
H(243)	2487(48)	10137(48)	56(26)	84(13)

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker WM-250 (250 MHz) instrument with TMS as internal standard. IR Spectra were taken on a Perkin-Elmer 577 instrument (KBr) and mass spectra on a Kratos MS-30 instrument (direct introduction of the sample, 70 eV, 250°C). Flash chromatography on a dry column [13] (Silufol 5/40 with benzene-ethyl acetate gradient elution) was used for separation of the mixtures. TLC was performed on Silufol UV-254 plates with the systems: ethyl acetate–benzene, 4:1* (A), benzene–ethyl acetate 9:1* (B), benzene–ethyl acetate, 2:1* (C), benzene–ethyl acetate, 4:1* (D), acetonitrile–benzene, 2:1* (E), or benzene–ethyl acetate, 1:1 (F). The cooling bath was acetone–dry ice with $CH_2Cl_2/CHCl_3$ and extracts were dried by filtration through glass wool.

Colorless crystals of the azapentalenone **5'** ($C_{18}H_{24}N_2O_4$) were prepared by slow crystallization from acetonitrile over 3 days. The crystals are orthorhombic: at 25°C: a = 9.310(5) Å, b = 10.907(6) Å, c = 17.344(8) Å; V = 1761(2) Å^3; d_{calc} = 1.254 g/cm^3; Z = 4; $P2_12_12_1$. 4242 Independent reflections were obtained on a Siemens P3/PC diffractometer with λMoKα = 0.71072 Å, graphite monochromator, and θ/2θ scanning , $\theta_{max} \leq 28°$. The structure was solved by a direct method and refined in a full matrix least squares analysis in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms were localized directly in difference Fourier synthesis and refined in the isotropic approximation. Final difference factors were $wR_2 = 0.1270$ for 2881 independent reflections (R_1 = 0.052 for 1754 independent reflections with $I > 2\sigma(I)$). Calculations were carried out on an PC/AT-586 IBM computer using the SHELXTL PLUS and SHELXL-93 programs [14].

Dioxolanones 1a,b were prepared according to the method in [4].

3-Benzyl-4-hydroxy-4,5-dimethyl-5-(4-methyl-3-pentenyl)oxazolidin-2-one (3a). The dioxolanone **1a** (5.88 g, 30 mmol) was added with stirring to a suspension of benzylamine hydrochloride (**4a**) (4.60 g, 32 mmol) and sodium hydroxide (1.28 g, 32 mmol) in water (10 ml). After 24 h at room temperature, the mixture was extracted with chloroform (25 ml, then 15 ml). The combined extracts were washed with water to neutral pH, filtered through glass wool, and the solvent was evaporated. The dark oil obtained was triturated with hexane (4 ml) with cooling. The crystals obtained were washed with hexane (3 ml) to give white crystals (7.35 g, 81%); mp 70-72°C. 0.51 g of the crystals were separated chromatographically to give 0.13 g (26%) of the first epimer and 0.30 g (58%) of the second epimer. The first epimer had mp 102-107°C and R_f 0.47 (system B) (twice). Mass spectrum, *m/z* (*I*, %): 303 (M^+ 6.7), 204 (26.2), 203 (62.8), 153 (47.8), 128 (21.5). IR spectrum, ν, cm^{-1}: 1730, 3350. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): (1.22 (3H, s), 1.45 (3H, s), 4,5-CH_3); (1.40-1.73 (2H, m), 2.30-2.50 (2H, m), 4-CH_2CH_2); (1.60 (3H, s), 1.66 (3H, s), CH=CC$\underline{H}_3)_2$); 3.87 (1H, s, 4-OH), (4.32 (1H, d, J = 15.0), 4.65 (1H, d, J = 15.0), 3-CH_2Ph); 5.06 (1H, t, C$\underline{H}$=C$(CH_3)_2$); 7.22-7.49 (5H, m, Ph). The second epimer had mp 84-87°C and R_f 0.25 (system B) (twice). The IR and mass spectrum of the second epimer agreed with those of the first epimer. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): (1.24 (3H, s), 1.33 (3H, s), 4,5-CH_3); (1.58-1.99 (2H, m), 2.07-2.23 (2H, m), 4-CH_2CH_2); (1.59 (3H, s), 1.66 (3H, s), CH=C(C$\underline{H}_3)_2$); 3.60 (1H, s, 4-OH), (4.33 (1H, d, J = 17.8), 4.66 (1H, d, J = 17.8), 3-CH_2Ph); 5.12 (1H, t, C$\underline{H}$=C$(CH_3)_2$); 7.25-7.48 (5H, m, Ph). The dehydration product from both epimers had the following data: ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): (1.51 (3H, s), 1.54 (3H, s), CH=C(C$\underline{H}_3)_2$); 1.70-2.16 (4H, m, 4-CH_2CH_2); 3.95 (1H, d, J = 3.7); 4.09 (1H, d, J = 3.7), 4.60 (1H, d, J = 15.5), 4.72 (1H, d, J = 15.5), 3-CH_2-Ph); 5.06 (1H, t, C$\underline{H}$=C$(CH_3)_2$); 7.24-7.40 (5H, m, Ph).

4-Hydroxy-4,5-dimethyl-5-(4-methyl-3-pentenyl)-3-[(2-pyridyl)methyl]oxazolidin-2-one (3b). A solution of 2-aminomethylpyridine (**2b**) (2.71 g, 25.1 mmol) in dichloromethane (5 ml) was added to a solution of dioxolanone **1a** (4.90 g, 25 mmol) in dichloromethane (15 ml) and held for 24 h at room temperature. The

* Plus 1-2 drops of cyclohexane.

reaction mixture was diluted with dichloromethane (10 ml), filtered through glass wool, and the solvent was evaporated. The light-brown oil was carefully dried in vacuo to yield a viscous oil (7.50 g, 99%) which was chromatographically pure (R_f 0.73, system E). Mass spectrum, *m/z*, (*I*, %): 304 (M^+ 1.1), 205 (53.0), 204 (89.4), 173 (52.7), 162 (56.0). IR spectrum, ν, cm^{-1}: 1750, 3360. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): (1.18 (3H, s), 1.29 (3H, s), 4,5-CH_3): (1.43-1.85 (2H, m), 1.97-2.20 (2H, m), 4-CH_2CH_2); (1.60 (3H, s), 1.68 (3H, s), CH=C(C$\underline{H}_3$)$_2$); (4.35 (1H, d, *J* = 17.6), 4.51 (1H, d, *J* = 17.6), 3-CH_2-2'-Py): 5.12 (1H, t, C$\underline{H}$=C(CH_3)$_2$); 6.34 (1H, s, 4-OH); 7.23-7.40 (2H, m, 3',5'-H_{Py}); 7.79 (1H, t, 4'-Py); 8.51 (1H, d, *J* = 5.3, 6'-H_{Py}).

3-(2-Cyanoethyl)-4-hydroxy-4,5-dimethyl-5-(4-methyl-3-pentenyl)oxazolidin-2-one (3c). The β-aminopropionitrile **2c** (2.10 g, 30 mmol) and 3-4 drops of triethylamine were added to a solution of the dioxolanone **1a** (5.88 g, 30 mmol) in dichloromethane (20 ml) and held for 144 h at room temperature. The solvent was evaporated and the residue was triturated with hexane (4 ml). The precipitate formed was washed with hexane (2 × 5 ml) and crystallized from ether–hexane (4:1) to yield white crystals (7.54 g, 95%); mp 93-102°C and R_f 0.54 (system F) (twice). Mass spectrum, *m/z* (*I*, %): 266 (M^+ 1.7), 167 (13.2), 166 (36.2), 125 (10.8), 108 (43.1). IR spectrum, ν, cm^{-1}: 1740, 3350. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): (1.25, 1.30 (3H, 2s), 1.34, 1.36 (3H, 2s), 4,5-CH_3); (1.46-1.76 (2H, m), 1.96-2.17 (2H, m), 4-CH_2CH_2), (1.57, 1.58 (3H, 2s), 1.62, 1.63 (3H, 2s), CH=C(C$\underline{H}_3$)$_2$); 2.60-2.75 (2H, m, 3-CH_2C$\underline{H}_2$CN); 3.35 (2H, t, 3-C$\underline{H}_2$$CH_2$CN); 5.03-5.17 (1H, m, C$\underline{H}$=C($CH_3$)$_2$); 6.11 (1H, s, 4-OH).

3-Allyl-4-hydroxy-4,5,5-trimethyloxazolidin-2-one (3d). Allylamine **2d** (2.28 g, 40 mmol) was added to a solution of dioxolanone **1b** (5.12 g, 40 mmol) in dichloromethane (20 ml) with cooling to room temperature. After 12 h the solvent was evaporated and the partially crystallizing colorless oil was washed with hexane–benzene 10:1 (3 × 3 ml) to give white crystals (7.40 g, 100%); mp 50-52°C, R_f 0.35 (system F). Mass spectrum, *m/z* (*I*, %): 185 (M^+ 19.5), 168 (20.0), 167 (64.8), 127 (21.9), 123 (56.4). IR spectrum, ν, cm^{-1}: 1740, 3320. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): (1.36 (3H, s), 1.37 (3H, s), 1.47 (3H, s), 4,5,5-CH_3); 3.78-4.03 (2H, m, 3-CH_2=CHC$\underline{H}_2$); 3.91 (1H, s, 4-OH); 5.15 (1H, dd, *J* = 1.0, *J* = 9.6), 5.25 (1H, dd, *J* = 1.0, *J* = 18.4),3-C$\underline{H}_2$=CHCH_2); 5.80-6.00 (1H, m, 3-CH_2=C$\underline{H}$$CH_2$).

3-Allyl-4-hydroxy-4,5-dimethyl-5-(4-methyl-3-pentenyl)oxazolidin-2-one (3e). Allylamine (**2d**) (1.71 g, 30 mmol) was added to a solution of the dioxolanone **1a** (5.88 g, 30 mmol) in dichloromethane (20 ml). After 96 h at room temperature, the solvent was evaporated, hexane (10 ml) was added with trituration and cooling, and the precipitated crystals were washed with hexane (3 × 3 ml) to give snow-white crystals (4.80 g, 63%). The substance did not have a sharp mp but melted in the range 40-70°C; R_f 0.22, 0.47 (system D) (twice). Mass spectrum, *m/z* (*I*, %): 253 (M^+ 2.9), 154 (35.6), 111 (64.5), 108 (72.5), 85 (34.7). IR spectrum, ν, cm^{-1}: 1725, 3330. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz); (1.36 (3H, s), 1.42 (3H, s), 4,5-CH_3); 1.50-1.78 (2H, m), 2.03-2.28 (2H, m), 4-CH_2CH_2); (1.60 (3H, s), 1.69 (3H, s), CH=C(C$\underline{H}_3$)$_2$); 3.78-4.00 (2H, m, 3-CH_2=CHC$\underline{H}_2$); 3.87 (1H, s, 4-OH); 5.08 (1H, t, C$\underline{H}$=C(CH_3)$_2$); (5.15 (1H, dd, *J* = 1.0, *J* = 8.8), 5.22 (1H, dd, *J* = 1.0, *J* = 17.7), 3-C$\underline{H}_2$=CHCH_2); 5.62-5.92 (1H, m, 3-CH_2=C$\underline{H}$$CH_2$).

3-Dimethylamino-4-hydroxy-4,5-dimethyl-5-(4-methyl-3-pentenyl)oxazolidin-2-one (3g). Dioxolanone **1a** (5.40 g, 27.55 mmol) was added to N,N-dimethylhydrazine **2f** (2.07 g, 34.44 mmol) with cooling to room temperature and triethylamine (2 ml) was added. After 96 h at room temperature the crystals were dissolved in benzene (10 ml). The solvent and traces of **2f** and triethylamine were evaporated at 50-60°C under reduced pressure. The pasty precipitate was mixed with ether (10 ml) with vigorous stirring at 7-10°C and filtered. The product was washed with cold ether (3 × 5 ml) to give 3.52 g of **3g** as white, scaly crystals. The combined mother liquors were allowed to evaporate in air to give an additional 0.52 g of **3g** and overall yield of white crystals of 4.04 g (57%); mp 84-87°C, R_f 0.43 (system C). Mass spectrum, *m/z* (*I*, %): 256 (M^+ 3.5), 151 (18.5), 104 (31.6), 87 (22.0), 86 (100.0). IR spectrum, ν, cm^{-1}: 1710, 3320. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz); (1.32 (3H, s), 1.46 (3H, s), 4,5-CH_3); (1.61 (3H, s), 1.69 (3H, s), CH=C(C$\underline{H}_3$)$_2$); (1.70-1.90 (2H, m), 2.05-2.18 (2H, m) 4-CH_2CH_2); 2.85 (6H, s, N(CH_3)$_2$); 5.11 (1H, t, C$\underline{H}$=C(CH_3)$_2$).

4-Hydroxy-4,5-dimethyl-5-(4-methyl-3-pentenyl)-3-(1,2,4-triazol-4-yl)oxazolidin-2-one (3h). A mixture of the 4-amino-1,2,4-triazole **2g** (1.68 g, 20 mmol), dioxolanone **1a** (3.96 g, 20.2 mmol), triethylamine (0.5 ml) and DMF (0.5 ml) was heated under reflux for 24 h at 110°C, and then cooled to room temperature. The reaction mixture was triturated with ether (10 ml) to give crystals which were washed with ether (4 × 5 ml). A white powder was obtained (2.15 g, 38%); mp 122-129°C, *Rf* 0.40, 0.85 (system A). Mass spectrum, *m/z* (*I*, %): 280 (M^+ 1.5), 151 (20.0), 129 (15.0), 111 (18.3), 110 (32.6). IR spectrum, ν, cm^{-1}: 1770, 3320. ^{1}H NMR spectrums (DMSO-d_6), δ, ppm (*J*, Hz): (1.27, 1.28 (3H, 2s), 1.48, 1.53 (3H, 2s), 4,5-CH_3); (1.67 (3H, s), 1.69 (3H, s), CH=C(C$\underline{H}_3$)$_2$); (1.70-1.98 (2H, m), 2.00-2.25 (2H, m), 4-CH_2CH_2); 5.16 (1H, t, C$\underline{H}$=C(CH_3)$_2$); 7.00 (1H, s, 4-OH); 8.68 (2H, s, 3',5'-H_{Het}).

4-Hydroxy-4,5-dimethyl-5-(4-methyl-3-pentenyl)-3-[(3-pyridyl)methyl]oxazolidin-2-one (3i). A solution of 3-aminomethylpyridine **2h** (2.71 g, 25.1 mmol) in dichloromethane (5 ml) was mixed with a solution of the dioxolanone **1a** (4.90 g, 25 mmol) in dichloromethane (15 ml). After holding for 72 h at room temperature the reaction mixture was diluted with dichloromethane (10 ml). The solution was filtered through glass wool. After evaporation of solvent, the substance formed was crystallized from benzene–hexane 4:1 (9.5 ml) to yield a yellow powder (6.76 g, 89%); mp 93-102°C, R_f 0.20, 0.45 (system E). Mass spectrum, *m/z* (*I*, %): 276 (M^+ 8.4), 204 (29.2), 111 (14.1), 94 (10.5), 93 (100.0). IR spectrum, ν, cm^{-1}: 1770, 3320. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): (1.21, 1.23 (3H, 2s), 1.30 (3H, s), 4,5-CH_3); (1.42-1.63 (2H, m), 1.92-2.17 (2H, m), 4-CH_2CH_2); (1.44, 1.50 (3H, 2s), 1.60, 1.62 (3H, 2s), CH=C(C$\underline{H}_3$)$_2$); (4.30 (1H, d, *J* = 17.3), 4.63 (1H, d, *J* = 17.3), 3-CH_2-3'-Py); 5.10 (1H, t, C$\underline{H}$=C(CH_3)$_2$); 6.10 (1H, s, 4-OH), 7.36 (1H, t, 5'-H_{Py}), 7.62 (1H, d, *J* = 7.8, 4'-H_{Py}); 7.98 (1H, d, *J* = 6.2 Hz, 6'-H_{Py}); 8.56 (1H, t, 2'-H_{Py}).

General Method for the Preparation of the Azapentalenones 4 and 5. The corresponding oxazolidinone **3** (2-10 mmol) was dried under vacuo over P_2O_5 for one day, dissolved in absolute formic acid (3 ml of the acid to 0.1 g of **3** if no other ratio is indicated), and the mixture was allowed to stand for the necessary time at room temperature (TLC monitoring). The acid was evaporated under reduced pressure, and the reaction mixture was dissolved in chloroform or dichloromethane (8-10 mmole of the mixture per 100 ml of solvent). The product was washed with a saturated solution of sodium bicarbonate (20 ml), saturated sodium chloride solution (20 ml) and then with water (20 ml). The solution was then filtered through glass wool and the solvent evaporated. After these general stages a specific purification of the reaction mixture followed.

3-Benzyl-3a,6a-dimethyl-4-isopropenylhexahydro-1-oxa-3-azapentalen-2-one (4a) was obtained by the general method from the oxazolidinone **3a** (1.82 g, 6 mmol) over 168 h. The reaction mixture was triturated with hexane (4 ml) with cooling and the crystals formed were washed with hexane (4 × 5 ml) to give a white powder (1.10 g, 65%); mp 90-92°C, R_f 0.48 (system B). Mass spectrum, *m/z* (*I*, %): 285 (M^+ 2.5), 204 (12.7), 203 (51.7), 92 (19.8), 91 (100.0). IR spectrum, ν, cm^{-1}: 1640, 1735. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): (1.10 (3H, s), 1.33 (3H, s), 1,4$_a$-CH_3); (1.48-1.73 (2H, m), 1.92-2.08 (1H, m), 2.17 (1H, dd), 2.32 (1H, dd) 5-7-H); 1.90 (3H, s, 5-C(CH_2)(C$\underline{H}_3$)); 4.02 (1H, d, *J* = 17.4), 4.82 (1H, d, *J* = 17.4), 4-CH_2Ph); (4.48 (1H, d, *J* = 1.0), 5.08 (1H, d, *J* = 1.0), 5-C(C$\underline{H}_2$(CH_3)); 7.18-7.24 (5H, m, Ph). Found, %: C 75.98; H 8.10; N 4.92. $C_{18}H_{23}NO_2$. Calculated, %: C 75.75; H 8.12; N 4.91.

3-(2-Cyanoethyl)-4-isopropenyl-3a,6a-dimethylhexahydro-1-oxa-3-azapentalen-2-one (4b) was prepared from oxazolidinone **3c** (2.13 g, 8 mmol) over 72 h. The reaction mixture was triturated with hexane (4 ml) with cooling and the crystals formed were washed with hexane (4 × 5 ml) to give white crystals (1.90 g, 96%); mp 91-93°C, R_f 0.53 (system F). Mass spectrum, *m/z* (*I*, %): 248 (M^+ 2.2), 167 (51.7), 166 (100.0), 126 (34.7), 123 (27.4). IR spectrum, ν, cm^{-1}: 1640, 1725, 2263. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): (1.35 (3H, s), 1.42 (3H, s), 1,4a-CH_3); (1.52-1.86 (3H, m), 1.87-2.08 (1H, m), 2.35 (1H, dd), 5-7-H); 1.80 (3H, s, 5-C(CH_2)(C$\underline{H}_3$)); 2.54-2.88 (2H, m, 4-CH_2C$\underline{H}_2$); (3.08-3.22 (1H, m), 3.25-3.35 (1H, m) 4-C$\underline{H}_2CH_2$); (4.90 (1H, d, *J* = 1.0), 5.00 (1H, d, *J* = 1.0), 5-C(C$\underline{H}_2$(CH_3)). Found, %: C 67.51; H 8.14; N 11.31. $C_{14}H_{20}N_2O_2$. Calculated, %: C 67.71; H 8.12; N 11.28.

3-Allyl-4-isopropenyl-3a,6a-dimethylhexahydro-1-oxa-3-azapentalen-2-one (4c) was prepared from the oxazolidinone **3e** (2.02 g, 8 mmol) over 95 h. The reaction product was triturated with hexane (4 ml) with cooling and the crystals which precipitated were washed with hexane (4 × 5 ml) to give a white powder (0.57 g, 30%). The substance did not show a sharp mp but melted in the range 51-64°C, R_f 0.60 (system D). Mass spectrum, *m/z*, (*I*, %): 235 (M^+ 2.5), 153 (18.4), 152 (76.0), 122 (13.9), 112 (27.4). IR spectrum, ν, cm^{-1}: 1640, 1730. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): (1.33 (3H, s), 1.37 (3H, s), 1,4a-CH_3), (1.44-1.70 (2H, m), 1.84-2.00 (1H, m), 2.13 (1H, dd), 2.27 (1H, dd), 5-7-H); 1.80 (3H, s, 5-C(CH_2)($C\underline{H}_3$); (3.50 (1H, dd, *J* = 7.4, *J* = 14.7), 4.02 (1H, m), 4-CH_2=CH$C\underline{H}_2$); (4.92 (1H, d, *J* = 1.0), 5.00 (1H, d, *J* = 1.0), 5-C($C\underline{H}_2$)(CH_3)); 5.08 (2H, dd, *J* = 1.0, *J* = 5.9), 5.15 (1H, dd, *J* = 1.0, *J* = 14.0), 4- $C\underline{H}_2$=CHCH_2); 5.70-5.88 (1H, m, 4-CH_2=C$\underline{H}CH_2$).

3-(2-Formyloxyethyl)-4-isopropenyl-3a,6a-dimethylhexahydro-1-oxa-3-azapentalen-2-one (4d). A solution of dioxolanone **1a** (1.74 g, 8.87 mmol) and ethanolamine **2e** (0.54 g, 8.87 mmol) in dichloromethane (15 ml) was allowed to stand for 48 h at room temperature (TLC monitoring) and the solvent was evaporated. The dried residue (**3f**) was dissolved in absolute formic acid and left for 48 h at room temperature. The mixture was then worked up as described in the general method. The product obtained was purified as in the case of **4b** to give 1.63 g, (69%) of white crystals; mp 69-71°C, R_f 0.54 (system F). Mass spectrum, *m/z*, (*I*, %): 267 (M^+ 1.7), 186 (20.7), 185 (59.2), 140 (13.0), 96 (26.8). IR spectrum, ν, cm^{-1}: 1640, 1720. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): (1.36 (3H, s), 1.37 (3H, s), 1,4a-CH_3); (1.45-1.60 (2H, m), 1.90 (1H, dd), 2.13 (1H, dd), 2.39 (1H, dd), 5-7-H); 1.88 (3H, s, 5-C(CH_2)($C\underline{H}_3$)); (3.11-3.27 (1H, m), 3.52-3.66 (1H, m), 4-$CH_2C\underline{H}_2$OCOH); 4.20-4.35 (2H, m, 4-$C\underline{H}_2CH_2$OCOH); (4.91 (1H, d, *J* = 1.0), 5.01 (1H, d, *J* = 1.0), 5-C($C\underline{H}_2$)(CH_3)); 8.05 (1H, s, 4-CH_2CH_2OCO$\underline{H}$). Found, %: C 63.08; H 7.94; N 5.22. $C_{14}H_{21}N_2O_4$. Calculated, %: C 62.90; H 7.92; N 5.24;

3-Dimethylamino-4-isopropenyl-3a,6a-dimethylhexahydro-1-oxa-3-azapentalen-2-one (4e) was prepared from oxazolidinone **3e** (2.56 g, 10 mmol) in formic acid (34 ml) over 120 h at room temperature. The colorless viscous product was dissolved in boiling hexane (10 ml) and allowed to cool and it crystallized over 24 h at room temperature. The precipitated crystals were filtered off and washed with hexane (3 × 2 ml) to give **4e** (1.0 g). The washings and mother liquors were combined. The liquors from two experiments were evaporated and the residue (1.44 g) was purified by chromatography followed by recrystallization from hexane (2 ml) and washing with cold hexane (2 × 1 ml) to give **4e** (0.62 g, 43% of the weight of evaporated liquors) as a white powder (**4e**). The overall yield from one experiment is 1.00 + 0.62/2 = 1.31 g (55%); mp 111-113°C, R_f 0.4 (system C). Mass spectrum, *m/z* (*I*, %): 238 (M^+ 11.8), 196 (13.6), 145 (13.7), 137 (50.1), 125 (11.1). IR spectrum, ν, cm^{-1}: 1640, 1735. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (J, Hz): (1.34 (3H, s), 1.49 (3H, s), 1,4a-CH_3); 1.50-1.94 (5H, m), 5-7-H); 2.00 (3H, s, 5-C(CH_2)($C\underline{H}_3$)), (2.73 (3H, s), 2.80 (3H, s), N(CH_3)$_2$); (4.86 (1H, d, *J* = 1.0), 4.93 (1H, d, *J* = 1.0), 5-C($C\underline{H}_2$)(CH_3)). Found, %: C 65.31; H 9.32; N 11.78. $C_{13}H_{22}N_2O_2$. Calculated, %: C 65.51; H 9.30; N 11.75.

4-*cis,trans*-Isopropenyl-3a,6a-dimethyl-3-[(2-pyridyl)methyl]hexahydro-1-oxaazapentalen-2-one (4f'/4f''), 3a,6a-Dimethyl-4-*endo*-(methyl-1-formyloxyethyl)-3-[(2-pyridyl)methyl]hexahydro-1-oxaaza-pentalen-2-one (5') and its *exo* isomer 5'' were obtained by the general method from oxazolidinone **3b** (2.13 g, 7.29 mmol) over 48 h as a dark viscous oil (2.40 g) showing three spots on TLC (R_f 0.56 for **4',4''**, 0.45 for **5'**, and 0.3 for **5''**, system F). The product was triturated with a mixture of ether–hexane (1:1, 10 ml). The solvent was cooled, decanted off and these two operations were repeated three more times to yield 1.17 g of crystals. Crystallization from ether–hexane gave **5'** (0.86 g, 38%) as slightly brownish crystals. The combined liquors were evaporated and the residue was separated by chromatography to give **4f'/4f''** (0.62 g, 31%, as an oil) and **5''** (0.58 g, 26%, as an oil). The overall yield of **4f'/4f''**, **5'** and **5''** was 95%.

Azapentalenones 4f'/4f'' ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): (1.09, 1.21 (3H, 2s), 1.49 (3H, s), 1,4a-CH_3); 1.05-2.48 (5H, m, 5-7-H); 1.61, 1.89 (3H, 2s, 5-C(CH_2)($C\underline{H}_3$)), {[4.13 (d, *J* = 16.7), 4.62 (d, *J* = 16.7)], [4.49 (d, *J* = 16.7), 4.85 (d, *J* = 16.7)], 2H 4-CH_2-2-Py}; (4.95 (1H, d, *J* = 1.0), 5.06 (1H, d, *J* = 1.0), 5-C($C\underline{H}_2$)(CH_3))); 7.16-7.32 (2H, m, 3',5'-H_{Py}); 7.66-7.80 (1H, m, 4'-H_{Py}); 8.41-8.56 (1H, m, 6'-H_{Py}).

Azapentalenone 5' Mp 144-146°C. Mass spectrum, *m/z* (*I*, %): 332 (M^+ 0.4), 287 (5.1), 243 (1.1), 227 (1.1), 204 (18.4). IR spectrum, ν, cm^{-1}: 1745. ^1H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): (1.24 (3H, s), 1.40 (3H, s), 1,4a-CH_3); (1.52 (3H, s), 1.63 (3H, s), 5-C($C\underline{H}_3$)$_2$OCHO); (1.60-1.80 (3H, m), 1.90-2.10 (1H, m), 2.16-2.30 (1H, m), 5-7-H); (4.40 (1H, d, *J* = 16.1), 4.56 (1H, d, *J* = 16.1), 4-CH_2-2-Py); 7.21 (1H, dd, *J* = 5.6, *J* = 8.1, 4'-H_{Py}); 7.30 (1H, d, *J* = 8.1, 3'-H_{Py}); 7.72 (1H, t, 5'-H_{Py}); 8.36 (1H, s, 5-C(CH_3)$_2$OCO$\underline{H}$); 8.48 (1H, d, *J* = 6.4, 6'-H_{Py}). Found, %: C 65.23; H 7.26; N 8.41. $C_{18}H_{24}N_2O_4$. Calculated: C 65.04; H 7.28; N 8.43.

Azapentalenone 5'' The mass spectrum of this compound was identical to that of **5'**. IR spectrum, ν, cm^{-1}: 1730. ^1H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): (1.26 (3H, s), 1.36 (3H, s), 1,4a-CH_3); (1.50-1.70 (1H, m), 1.80-2.20 (3H, m). 2.52 (1H, dd), 5-7-H); (1.51 (3H, s), 1.59 (3H, s), 5-C($C\underline{H}_3$)$_2$OCOH); (4.48 (1H, d, *J* = 21.9), 4.60 (1H, d, *J* = 21.9), 4-CH_2-2-Py); 7.24 (1H, dd, *J* = 6.6, *J* = 9.8, 4'-H_{Py}); 7.36 (1H, d, *J* = 9.8, 3'-H_{Py}), 7.71 (1H, t, 5'-H_{Py}); 8.16 (1H, s, 5-C(CH_3)$_2$OCO$\underline{H}$); 8.50 (1H, d, *J* = 5.5, 6'-H_{Py}).

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