1,3-Dipolar Addition of Formonitrile Oxide and Hydroxyiminoacetonitrile Oxide to Some Olefins. The Synthesis of Isoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazolines (1).

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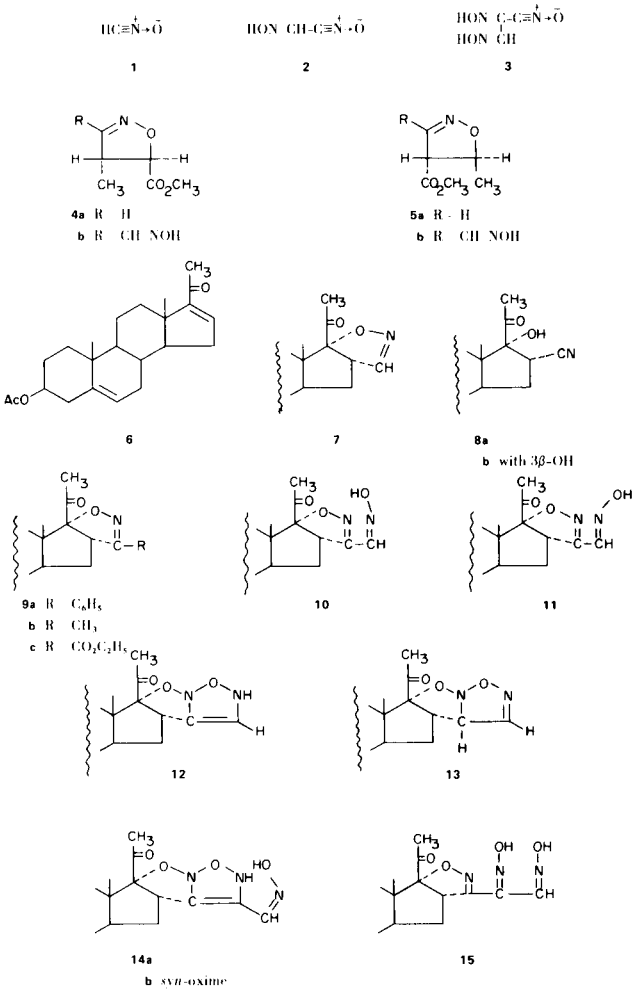
The 1,3-dipolar addition of formonitrile oxide and hydroxyiminoacetonitrile oxide to a variety of olefins is described. The 3-*anti*-aldoximino-Δ^2-isoxazolines, resulting from the addition of the dimeric hydroxyiminoacetonitrile oxide to the olefinic substrate, undergo base-catalyzed cyclization to yield novel isoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazolines. The latter products are rearranged to α-oximino-γ-lactones after additional treatment with base.

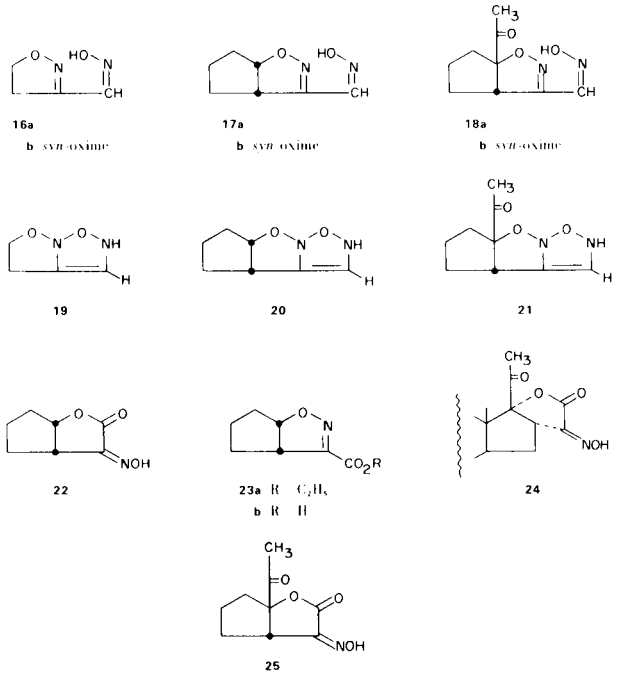
Olefins and acetylenes are converted into Δ^2-isoxazolines and isoxazoles, respectively, upon exposure to dilute solutions of the 1,3-dipole formonitrile oxide (**1**) (3). The dimerization of **1** to yield hydroxyiminoacetonitrile oxide (**2**) competes with the foregoing addition process and the resulting dimer in turn adds to olefinic substrates to give aldoximino substituted adducts. Thus methyl crotonate and **1** yield a mixture of the isoxazolines **4a**,**b** and **5a**,**b**, the oximino products being formed by the addition of the dimeric 1,3-dipole **2** to the unsaturated ester (4). This communication describes the addition of formonitrile oxide (**1**) and the corresponding dimeric and trimeric 1,3-dipoles **2** and **3** to various olefins and the formation of the novel isoxazolidino[2,3-*d*]-Δ^3-1,2,5-oxadiazoline system from the dimeric and trimeric adducts.

Exposure of 3β-acetoxy-5,16-pregnadien-20-one (**6**) to an ethereal solution of formonitrile oxide (**1**), generated by treating sodium fulminate in an ether-water mixture with 20% sulfuric acid (3), gave a mixture consisting of three major components which was partially resolved by preparative tlc over silica gel. The least polar product, isolated in 16% yield was identified as the $\Delta^{2'}$-isoxazoline **7** on the basis of its spectroscopic properties and elemental analysis. The orientation and stereochemistry of this adduct follows from the formation of a mixture of 3β,17α-dihydroxy-16α-cyano-5-pregnen-20-one (**8a**) and its 3-acetate **8b** on treatment of **7** with dilute sodium hydroxide in methanol. This result is in accord with the observations of Culbertson, *et al.*, (5) who showed by chemical means that the $\Delta^{2'}$-isoxazolines resulting from the addition of benzonitrile oxide, acetonitrile oxide and carbethoxyformonitrile oxide to enone **6** have structures **9a-c**, respectively.

The $\Delta^{2'}$-isoxazoline **7** was recovered unchanged after exposure to a freshly prepared solution of formonitrile oxide (**1**). Hence the other products of this reaction are not formed simply by the addition of **1** to the isoxazoline double bond of **7**.

The second product (yield 46%) of intermediate polarity was the 3'-*anti*-aldoximino-$\Delta^{2'}$-isoxazoline **10**





which arises by addition of dimeric hydroxyiminoacetonitrile oxide (**2**) to the enone **6**. The nmr spectrum of **10** shows, in addition to the expected resonances for the steroid nucleus, a singlet at 7.30 ppm for the oxime methine-H and a broad singlet (exchangeable with deuterium oxide) at 9.27 ppm for the hydroxyl proton of the oxime. The stereochemistry and orientation of the oxazoline ring of **10** are the same as that of the unsubstituted adduct **7** because the 18-H resonances of **7** and **10** are 0.71 and 0.74 ppm, respectively. These data are in good agreement with the value reported for the 18-H resonance of the adduct **9b**, resulting from the normal addition of acetonitrile oxide to **6** (6). The 18-H resonance reported for the isomer of inverse addition of acetonitrile oxide to **6** is at 0.83 ppm (6).

When oxime **10** was heated at 210° for 30 seconds, it was partially converted into two less polar compounds which were separated by preparative tlc. The major product isolated in 47% yield was shown by nmr to be the *syn*-oxime **11**. The oxime methine-H appears as a singlet at 7.93 ppm, the resonance of this proton being shifted downfield by 0.63 ppm relative to the corresponding methine-H of the *anti*-oxime. The *syn*-oxime **11** was also obtained in moderate yield by treatment of the *anti*-oxime **10** with dilute hydrochloric acid in methanol. The second product from the thermolysis of **10**, isolated in 21% yield, is formulated as the novel isoxazolidino-[2,3-*b*]-Δ^3-1,2,5-oxadiazoline (**12**). The ir spectrum of **12** shows a broad weak band at 3500 cm^{-1} attributed to the NH group and its nmr spectrum shows a singlet at 8.12 ppm for the heterocyclic olefinic proton. Absence of resonance ascribable to a second low field proton excludes the isomeric Δ^2-structure **13**. Substance **12** was obtained more efficiently by brief exposure of **10** to dilute sodium methoxide in methanol.

The most polar fraction isolated from the addition of formonitrile oxide (**1**) and related species to **6** was a two component mixture which gave rise to a single product, m.p. 222-223° (6% yield), after repurification by preparative tlc and crystallization. An elemental analysis showed this substance to be an adduct derived from enone **6** and trimer **3**, the expressions **14** and **15** depicting the most probable structures. The nmr spectrum of the tris adduct in DMSO-d_6 shows sharp 1-proton singlets at 5.44 (NH) and 12.40 ppm (OH), which disappear on addition of deuterium oxide. These spectral results support the cyclized structure **14** rather than the dioxime **15**, the exchangeable protons of which would be expected to exhibit similar chemical shifts. In support of this conclusion J. P. Guetté, *et al.*, report that the OH resonances for a series of glyoximes occur in the range 11.48-12.06 ppm (7). This substance is assigned the *anti*-oxime structure **14a**, since it was isomerized to the *syn*-oxime **14b** on heating or on treatment with acid.

Experiments were next carried out with three simple olefins to investigate the cyclization of the resulting oximino-Δ^2-isoxazolines. Thus, reaction of ethylene, cyclopentene and 1-acetylcyclopent-1-ene with a solution of formonitrile oxide (**1**) furnished the respective unstable *anti*-oximes **16a-18a** as indicated by spectroscopic data and by transformation to the stable *syn*-oximes **16b-18b** by methanolic hydrochloric acid (see Table I). Brief treatment of the *anti*-oximes with dilute methanolic potassium hydroxide in chloroform provided the isoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazolines **19-21**, whose spectroscopic properties were in accord with the proposed structures.

Further treatment of the isoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazolines or their *anti*-oxime precursors with base led to rearrangement of these heterocyclic systems. Thus exposure of the *anti*-oxime **17a** to 1% methanolic potassium hydroxide afforded a new product, m.p. 147-148°, more polar by tlc than isoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazoline (**20**) (8). This product is assigned the α-oximino lactone structure **22** on the basis of the following evidence. The uv spectrum of **22** exhibits λ max 226 nm (ε 10,000) and its ir solution spectrum shows bands at 1775 and 1665 cm^{-1} attributed to the lactone carbonyl and C=N groups, respectively, as well as bands at 3570 cm^{-1} (unassociated OH) and 3250 cm^{-1} (associated OH) for the hydroxyl group of the oxime. These results are in harmony with the spectroscopic data reported for α-oximino-γ-butyrolactone (9) and various *syn*-α-

TABLE I

Physical and Analytical Data for Hydroxyiminoacetonitrile Oxide Adducts of Ethylene, Cyclopentene, 1-Acetylcyclopent-1-ene and Related Compounds.

Compound	M.p.	uv nm (ε)	ir cm^{-1}	nmr ppm	Empirical Formula	Analysis % Calcd.	Found
16a	106-107° (a)	255 (10,900)		7.85 (s, olefinic-H) (b) 14.08 (m, oxime-H)	$C_4H_6N_2O_2$	C 42.10 H 5.30 N 24.55	42.06 5.50 24.69
17a	105-106° (a)	256 (10,500)		7.38 (s, olefinic-H) 9.50 (broad s, oxime-H)	$C_7H_{10}N_2O_2$	C 54.53 H 6.54 N 18.17	54.76 6.66 18.57
18a	111-112° (a)	254 (10,400)		7.35 (s, olefinic-H) 9.30 (broad s, oxime-H)	$C_9H_{12}N_2O_3$	C 55.09 H 6.17 N 14.28	55.09 6.18 14.18
16b	166-167° (a)	252 (13,600)		8.58 (s, olefinic-H) (b) 14.08 (broad m, oxime-H)	$C_4H_6N_2O_2$	C 42.10 H 5.30 N 24.55	42.06 5.50 24.69
17b	142-143° (c)	252 (14,400)		8.07 (s, olefinic-H) 8.42 (s, oxime-H)	$C_7H_{10}N_2O_2$	C 54.53 H 6.54 N 18.17	54.62 6.59 18.24
18b	99-100° (a)	251 (12,000)		8.02 (s, olefinic-H) 8.92 (s, oxime-H)	$C_9H_{12}N_2O_3$	C 55.09 H 6.17 N 14.28	54.82 6.11 14.06
19	oil		3300 (NH) (d) 1650 (C=C) 1575	2.12 (m, NH) 8.31 (s, olefinic-H)	$C_4H_6N_2O_2$	C 42.10 H 5.30 N 24.55	42.02 5.24 24.38
20	oil		3350 (NH) 1640 (C=C) 1560	ca. 1.83 (m, NH) 8.29 (s, olefinic-H)	$C_7H_{10}N_2O_2$	C 54.53 H 6.54 N 18.17	54.57 6.50 18.02
21	oil		3350 (NH) 1700 (C=O) 1640 (C=C) 1560	3.98 (broad s, NH) 8.30 (s, olefinic-H)	$C_9H_{12}N_2O_3$	C 55.09 H 6.17 N 14.28	54.82 6.11 14.06

(a) Recrystallized from ethylacetate-hexane. (b) Spectrum measured in pyridine-d_5. (c) Recrystallized from methanol. (d) Spectrum recorded as film.

oximino ketones (10). The Δ^2-isoxazolino acid **23b** represents an alternate possibility for the rearrangement product. However, carboxyl-H-resonance is absent in the nmr spectrum and the foregoing spectral data do not support structure **23b**. In addition, the acid **23b** was prepared in an unambiguous manner by the addition of carboethoxynitrile oxide to cyclopentene followed by alkaline hydrolysis. The authentic acid **23b** exhibited m.p. 90-91° and was not identical with the product obtained by base-catalyzed rearrangement of the oxime **17**.

Similar treatment of oximes **10** and **18** and the corresponding isoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazolines **12** and **21** furnished the respective α-oximino lactones **24** and **25**.

EXPERIMENTAL (11)

Preparation of Formonitrile Oxide Solution (3).

A suspension of wet mercury fulminate (7 g.) in water (8 ml.) was cooled to 0° and treated with stirring with 8% sodium amalgam until the solution became clear. After separation of the mercury by decantation, the solution of sodium fulminate was covered with 80 ml. of ether and the mixture acidified with ice cold 20% sulfuric acid. The ether layer was separated and the aqueous phase was extracted again with 40 ml. of ether. The combined ether extracts were dried over magnesium sulfate, filtered, and then treated with the requisite olefin (see below).

Reaction of 3β-Acetoxy-5,16-pregnadien-20-one (**6**) with Formonitrile Oxide (**1**).

Compound **6** (1.2 g.) was added to the formonitrile oxide solution from the preceding experiment and after 20 hours, the reaction mixture was washed with dilute sodium bisulfite and

water, dried over magnesium sulfate and evaporated. The oily residue was purified by preparative tlc on silica gel (12) using benzene-ether (4:1) for development to yield in order of increasing polarity: (a) Δ^2-isoxazoline (**7**) (0.21 g., 16%), m.p. 191-192° (methanol); $[\alpha]_D$ + 65°; ir (chloroform): 1720, 1600, 1250, 1030 cm^{-1}; nmr: 0.71 (s, 18-H), 4.1 (m, 16β-H), 6.99 ppm (d, J 2 Hz, -CH=N-).

Anal. Calcd. for $C_{24}H_{33}NO_4$: C, 72.15; H, 8.33; N, 3.51. Found: C, 72.31; H, 8.81; N, 3.49.

(b) 3-*anti*-Aldoximino-Δ^2-isoxazoline (**10**) (0.65 g., 46%), m.p. 202-204° (ethyl acetate-hexane); $[\alpha]_D$ -61°; uv 256 nm (ε 9560); ir (chloroform): 3260, 1550, 1030 cm^{-1}; nmr 0.74 (s, 18-H), *ca.* 4.5 (m, 3α-H, 16β-H), 7.30 (s, -CH=N-), 9.27 ppm (m, oxime-H).

Anal. Calcd. for $C_{25}H_{34}N_2O_5$: C, 67.85; H, 7.75; N, 6.33. Found: C, 67.77; H, 7.60; N, 6.15.

(c) 3-*anti*-Aldoximinoisoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazoline (**14a**) (0.1 g., 6%-after 2nd preparative tlc of most polar fraction), m.p. 222-223° (chloroform-hexane); $[\alpha]_D$ -52°; uv: 243 nm (ε 3100); ir (nujol) 1700, 1680, 1260, 950 cm^{-1}; nmr (DMSO-d_6): 0.72 (s, 18-H), 4.3-4.6 (m, 3α-H, 16β-H), 5.44 (s, NH), 7.58 (s, -CH=N-), 12.40 ppm (s, oxime-H).

Anal. Calcd. for $C_{26}H_{35}N_3O_6$: C, 64.31; H, 7.27; N, 8.65. Found: C, 64.61; H, 7.22; N, 8.41.

Thermolysis of *anti*-Oxime **10**.

Substance **10** (0.32 g.) was heated at 210° for 30 seconds and cooled to 20°. The mixture was purified by preparative tlc on silica gel using benzene-ether (4:1) to yield in addition to recovered **10** (0.07 g., 21%): (a) *syn*-oxime **11** (0.15 g., 47%), m.p. 237-238° (methanol); $[\alpha]_D$ -74°; uv: 252 nm (ε 11,810); ir (chloroform): 3250, 1700, 1025 cm^{-1}; nmr: 0.73 (s, 18-H), 4.26 (m, 16β-H), 7.93 (s, -CH=N-), 8.52 ppm (s, oxime-OH).

Anal. Calcd. for $C_{25}H_{34}N_2O_5$: C, 67.85; H, 7.75; N, 6.33. Found: C, 68.07; H, 7.47; N, 6.20.

(b) Isoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazoline (**12**) (0.07 g., 21%), m.p. 220-225° (ethylacetate); $[\alpha]_D$ -60°; uv no absorption; ir (chloroform): 1725, 1030 cm^{-1}; nmr: 0.88 (s, 18-H), 3.32 (s, NH), 4.4-4.6 (m, 3α-H, 16β-H), 8.12 ppm (s, 3-olefinic-H).

Anal. Calcd. for $C_{25}H_{34}N_2O_5$: C, 67.85; H, 7.75; N, 6.33. Found: C, 67.99; H, 7.46; N, 6.27.

Synthesis of *syn*-Oxime **11**.

A solution of the *anti*-xoime **10** (0.3 g.) in methanol (25 ml.) containing 0.01 ml. of concentrated hydrochloric acid was kept for 1 hour at 20°. The reaction mixture was diluted with ether, washed with dilute sodium bicarbonate solution and water, dried over magnesium sulfate and evaporated. The crude product was purified by preparative tlc on silica gel using benzene-ether (4:1) to yield *syn*-oxime **11** (0.12 g., 40%), m.p. 236-238° identical by mixed m.p. and ir spectrum with the *syn*-oxime obtained from the preceding experiment.

Synthesis of 3-*syn*-Aldoximinoisoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazoline (**14b**).

A solution of the *anti*-oxime **14a** (0.15 g.) in methanol (5 ml.) containing 0.01 ml. of concentrated hydrochloric acid was kept for 40 minutes at 20°. The reaction mixture was processed as described in the preceding experiment and purified by preparative tlc over silica gel using benzene-ether (3:1) to yield 3'-*syn*-aldoxime **14b** (0.11 g., 73%), m.p. 209-211° (chloroform-hexane); $[\alpha]_D$ -42° (pyridine); uv: 240 nm (ε 4940); ir (chloroform): 3550, 3300, 1720, 1700 cm^{-1}; nmr (deuteriochloroform-d_5-pyridine): 0.65 (s, 18-H), 4.3-5.0 (m, 3α-H, 16β-H), 8.43 ppm (s, -CH=N-).

Anal. Calcd. for $C_{26}H_{35}N_3O_6$: C, 64.31; H, 7.29; N, 8.65. Found: C, 64.38; H, 7.32; N, 8.71.

Preparation of 3-*anti*-Aldoximino-Δ^2-isoxazolines (**16a**, **17a**, **18a**).

Ethylene was bubbled through a solution of formonitrile oxide **1**, prepared from 20 g. of mercury fulminate, for 18 hours after which time the reaction mixture was washed with dilute sodium bicarbonate and water, dried over magnesium sulfate and evaporated. The crude mixture was purified by preparative tlc over silica gel to yield **16a** (0.31 g.). Similar treatment of cyclopentene and 1-acetylcyclopent-1-ene gave the respective *anti*-oximes **17a** and **18a**. See Table I for analytical data.

Preparation of 3-*syn*-Aldoximino-Δ^2-isoxazolines (**16b**, **17b**, **18b**).

A solution of *anti*-oxime **16a** (0.04 g.) in methanol (4 ml.) containing 0.01 ml. of concentrated hydrochloric acid was kept for 18 hours at 20°. The reaction mixture was diluted with ether, washed with dilute sodium bicarbonate solution and water, dried over magnesium sulfate and evaporated to yield **16b** (0.03 g., 75%). See Table I for analytical data. Similar treatment of *anti*-oximes **17a** and **18a** gave the respective *syn*-oximes **17b** and **18b**. See Table I for analytical data.

Preparation of Isoxazolidino[2,3-*b*]-Δ^3-1,2,5-oxadiazolines (**19**, **20**, **21**).

A solution of the *anti*-oxime **16a** (0.12 g.) in chloroform (7 ml.) was treated with a solution of 1% potassium hydroxide in methanol (0.5 ml.). After 0.5 minutes the reaction mixture was diluted with ether, washed with water, dried magnesium sulfate) and evaporated. Purification of the residue by preparative tlc on silica gel using benzene-ether (7:3) furnished **19** (0.04 g., 33%) as an oil. Similar treatment of *anti*-oxime **17a** (0.15 g.) gave **20** (0.06 g., 40%). The cyclization of **18a** to **21** was accomplished by treating **18a** (0.28 g.) in methanol (7 ml.) with 1% potassium hydroxide (7 ml.) for 1 hour. Acetic acid (0.07 ml.) was added and the reaction mixture was evaporated to a volume of 5 ml. This solution was diluted with ether (50 ml.), washed with diltue sodium bicarbonate solution and water, dried over magnesium sulfate and evaporated. Purification fo the resulting product by preparative tlc on silica gel using benzene-ether (3:1) for development gave **21** (0.12 g., 42%) as an oil. See Table I for analytical data for **19**, **20**, **21**.

Conversion of *anti*-Oxime **18a** to α-Oximinolactone **25**.

The oxime **18a** (0.2 g.) was treated with a solution of 1% potassium hydroxide in methanol (8 ml.) for 15 minutes at 23°. The reaction mixture was acidified with concentrated hydrochloric acid, poured into water, and the product isolated by extraction with ethyl acetate. The resulting product was purified by preparative tlc on silica gel using benzene-ether (2:1) for development to yield **25** (0.04 g., 20%) m.p. 138-139° (ethyl acetate-hexane); uv: 226 nm (ε 10,500); ir (chloroform): 3550, 3200, 1785, 1725, 1660 cm^{-1}; nmr: 2.34 (s, acetyl-H), 3.79 ppm (m, methine-H).

Anal. Calcd. for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10. Found: C, 54.97; H, 5.69; N, 6.92.

Conversion of Isoxazolidino[2,3-*b*]-Δ^3-1,2,5-Oxadiazoline (**21**) to α-Oximinolactone **25**.

Compound **21** (0.07 g.) was treated with a solution of 1% potassium hydroxide in methanol (2.5 ml.) for 15 minutes at 23°. The reaction mixture was processed exactly as described in the preceding experiment to yield **25** (0.04 g., 57%), m.p. 138-139°,

identical in all respects with the product of the foregoing reaction.

Conversion of *anti*-Oxime **17a** to α-Oximinolactone **22**.

The *anti*-oxime **17a** (0.2 g.) was treated with a solution of 1% potassium hydroxide in methanol (7.5 ml.) for 30 minutes at 23°. The reaction mixture was processed exactly as described for the conversion of **21** into **25** to give **22**, (0.11 g., 55%), m.p. 147-148° (ethylacetate-hexane); uv: 225 nm (ε 10,820); ir (chloroform): 3560, 3350, 1770, 1650 cm^{-1}; nmr: 3.67 (m, methine-H), 5.16 ppm (m, OCH).

Anal. Calcd. for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.03; H, 5.92; N, 9.06.

Conversion of *anti*-Oxime **10** to α-Oximinolactone **24**.

anti-Oxime **10** (0.3 g.) was dissolved in methanol (25 ml.) and treated with a solution of 10% potassium hydroxide in methanol (0.1 ml.). The reaction mixture was stirred until the precipitate of **12**, which formed shortly after the addition of base had dissolved completely. Ether (200 ml.) was added and the solution was washed with dilute hydrochloric acid and dilute sodium bicarbonate solutions, then with water, dried over magnesium sulfate and evaporated. The product was purified by prepared tlc on silica gel using benzene-ether (65:35) for development to yield **24** (0.13 g., 43%), m.p. 184-187° (ethyl acetate-hexane); uv: 241 nm (ε 7900); ir (chloroform) 3550, 3250, 1790, 1725, 1600 cm^{-1}; nmr: 0.73 (s, 18-H), 4.05 (m, 16β-H), 11.64 ppm (broad m, oxime-H).

Anal. Calcd. for $C_{25}H_{33}NO_6$: C, 67.70; H, 7.50; N, 3.16. Found: C, 67.91; H, 7.62; N, 3.18.

3-Carboethoxy-5,6-dihydro-4*H*-cyclopent[*d*]-Δ^2-isoxazoline (**23a**).

A solution of chloroximino ethyl acetate (13) (3 g.) and cyclopentene (3 ml.) in dry ether (25 ml.) was treated dropwise with stirring with a solution of triethylamine (2 g.) in dry ether (7 ml.). After the addition, the reaction mixture was stirred for 4 hours and partitioned between ether and water. The organic phase was washed with dilute hydrochloric acid and dilute potassium bicarbonate solutions and water, dried over magnesium sulfate and evaporated. A benzene solution of the residual oil (3.5 g.) was filtered through a column of silica gel (100 g.) to yield pure **23a** after evaporation of the solvent (2.8 g., 45%); uv: 247 nm (ε 5320); ir (film): 1720, 1625, 1580 cm^{-1}; nmr: 1.35 (t, J7 Hz, CH_3CH_2-), 3.83 (t of d, J10,9.2 Hz, methine-H), 4.31 (q, J7 Hz, CH_3CH_2-), 5.18, 5.27 (ppm) (pair d, J10,4 Hz, -CHO-).

Anal. Calcd. for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 58.54; H, 6.85; N, 7.48.

3-Carboxy-5,6-dihydro-4*H*-cyclopent[*d*]-Δ^2-isoxazoline (**23b**).

A mixture of ethyl ester **23a** (1 g.) and water (2.6 ml.) containing sodium hydroxide (0.22 g.) was stirred at 5° for 45 minutes. The resulting solution was treated with concentrated hydrochloric acid (1 ml.) and extracted with 3 x 20 ml. portions of ether. The organic phase was washed with water, dried over magnesium sulfate and evaporated to yield **23b** (0.81 g., 96%), m.p. 90-91° (benzene-petroleum ether); uv 242 nm (ε 5320); ir (potassium bromide): 3450 (broad), 1710, 1575 cm^{-1}; nmr 3.84 (t of d, J10, 9.2 Hz, methine-H), 5.25, 5.37 (paid of d, J10, 4 Hz, -CHO-), 10.38 ppm (s, carboxyl-H).

Anal. Calcd. for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.12; H, 5.99; N, 9.07.

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(12) Preparative tlc was conducted using silica gel HF (From Brinkmann Instruments, Inc., N.Y.) at thicknesses of 1.3 mm and compound loadings of 2 mg./cm.

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