Alkyl Nitrate Nitration of Active Methylene Compounds. Nitration of 2-Substituted 2-Oxazolines [1]

Henry Feuer*, Hanamanthsa S. Bevinakatti [2] and Xuan-Gan Luo [3]

Richard B. Wetherill Laboratory, Purdue University,
West Lafayette, Indiana 47907

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2-Alkyl- and 2-aralkyl-2-oxazolines are readily converted to the corresponding α-nitroalkyl- and α-nitroaralkyl-2-oxazolines on treatment with an alkali metal amide such as potassium or sodium amide in liquid ammonia or with lithium diisopropylamide (LDA) in THF and an alkyl nitrate. Tertiary nitro compounds, such as 2-(2-nitro-2-propyl)-4,4-dimethyl-2-oxazoline (**16**) and 2-(diphenylnitromethyl)-4,4-dimethyl-2-oxazoline (**17**) are obtained in good yield when the anions of 2-(2-propyl)-4,4-dimethyl-2-oxazoline (**14**) and of 2-(diphenylmethyl)-4,4-dimethyl-2-oxazoline (**23**), generated by LDA are added to the nitrate in THF (inverse addition). The spectral data of the primary and secondary α-nitroalkyl- and α-nitroaralkyl-2-oxazolines reveal that they exist mostly in their dipolar structure. These compounds are readily converted to the corresponding α-halonitro-2-oxazolines on treatment with potassium hypobromite or hypochlorite.

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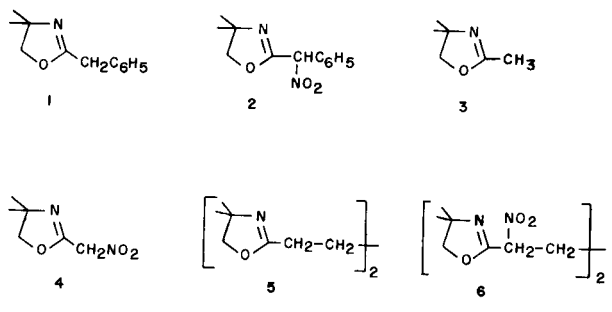

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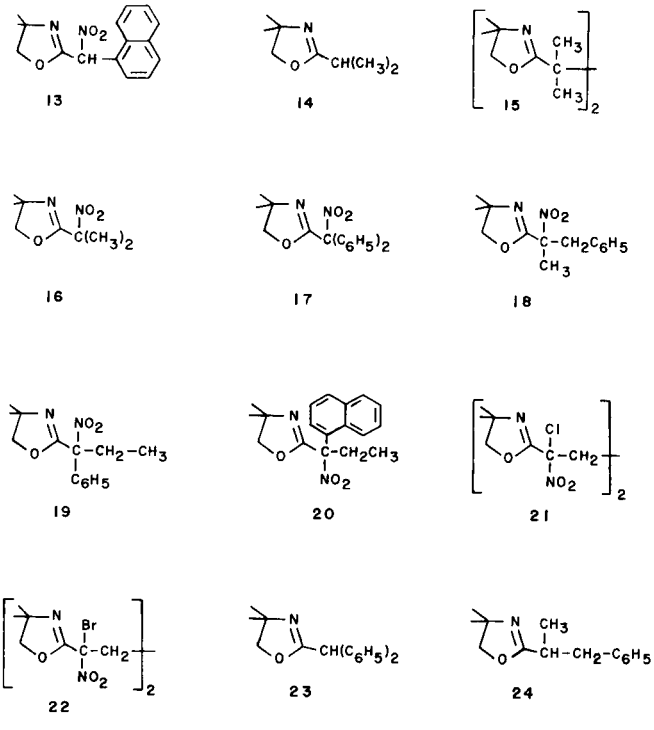
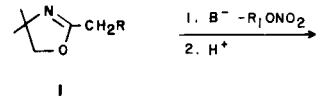


In continuation of our studies to introduce the nitro group into heterocyclics [4] by alkyl nitration, we now report our results with 2-oxazolines. This system was chosen because it has been shown to constitute valuable reaction intermediates [5a-i]. Ring opening reactions of 2-nitroalkyl- and 2-nitroaralkyl-2-oxazolines which resulted from the alkyl nitration are being investigated and will be reported in a subsequent paper.



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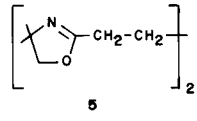
The nitration reaction in eq 1 was studied in several base-solvent systems with 2-benzyl-4,4-dimethyl-2-oxazoline (**1**, R = C_6H_5) as a model compound. As shown

in Table 1, the highest yield of 2-(α-nitrobenzyl)-4,4-dimethyl-2-oxazoline (**2**, R = C_6H_5) (86%) was obtained in the potassium amide-liquid ammonia system (A) when the molar ratio of **1** to base to nitrating agent was 1:2:2.2 and when 15 minutes was allowed for both anion formation and nitration. In the LDA-THF system (B) the yield was only 56%.

In order to determine the scope of the reaction 2-oxazolines of varied structures were nitrated. As can be seen from the results which are summarized in Table 2, systems A and B were not equally effective in providing optimum yields. For example, the nitration of 2,4,4-trimethyl-2-oxazoline (**3**) in systems A and B afforded 2-nitromethyl-4,4-dimethyl-2-oxazoline (**4**, R = H) in 13% and 65% yields, respectively. On the other hand, in the nitration of 1,4-bis[2-(4,4-dimethyl-2-oxazolinyl)]butane (**5**), the yield of 1,4-dinitro-1,4-bis[2-(4,4-dimethyl-2-oxazolinyl)]butane (**6**) was 55% in system A and only 15% in system B (eq 2). In general, the yield of nitrated products



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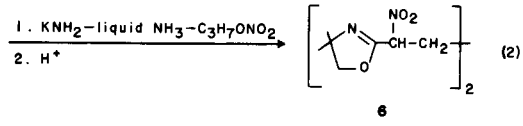

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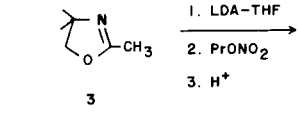
(2)

was increased when the alkyl nitrate was added as fast as the exotherm permitted. For example, in the nitration of 2-(2-cyclohexylethyl)-4,4-dimethyl-2-oxazoline (**7**) addition of propyl nitrate over 12 and 17 minutes, afforded 2-(1-nitro-2-cyclohexylethyl)-4,4-dimethyl-2-oxazoline (**8**) in yields of 58% and 32%, respectively.

It is noteworthy that the nitration of **3** was successful only when both anion formation and addition of the alkyl nitrate were carried out at -75°. In addition to compound **4**, 1,2-dinitro-1,2-bis[2-(4,4-dimethyl-2-oxazolinyl)]ethane (**9**) was also formed in 5% yield (eq **3**). The structure of **9** was established by its spectral data.



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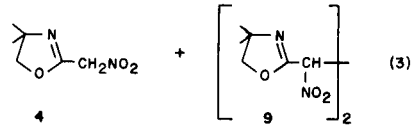

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(3)

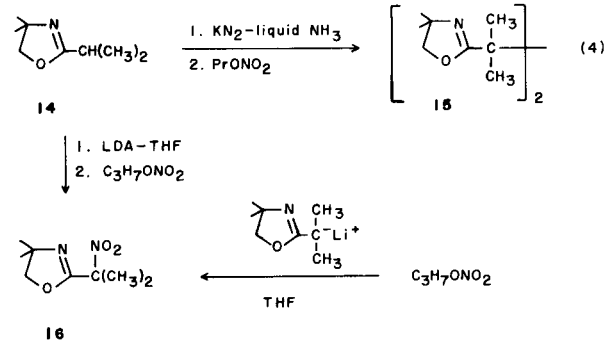
Table 1

Effect of Various Base-Solvent Systems on the Yield of 2-(α-Nitrobenzyl-4,4-dimethyl-2-oxazoline (**2**)

Base-Solvent	**2**, yield %	Recovery of **1**, %
Potassium amide-liquid ammonia [a]	84 [b]	–
Sodium amide-liquid ammonia [a]	75 [b]	–
BuLi-THF [c]	31 [d]	57
LDA-THF [e]	56 [f]	20

[a] The molar ratio of **1** to base to propyl nitrate was kept at 1:2:2.2 in approximately 250 ml of solvent. Anion formation and nitration were performed at about -33°. [b] Obtained on acidification of an aqueous solution of the potassium or sodium salt of **2** with acetic acid. [c] The molar ratio of **1** to base to propyl nitrate was kept at 1:1.1:1. Anion formation was done at -78° and nitration at -30°. [d] Doubling the molar ratios of BuLi and propyl nitrate did not alter the yield of **2**. [e] The molar ratio of **1** to base to propyl nitrate was 1:1.5:1.5. Anion formation was performed at 0° and nitration at -25°. [f] Nitration at 0° gave 42% of **2** and 57% recovery of **1**.

Nitration of 2-(2-propyl)-4,4-dimethyl-2-oxazoline (**14**) in system A did not afford the expected tertiary nitro compound 2-(2-nitro-2-propyl)-4,4-dimethyl-2-oxazoline (**16**); instead a dimer, 2,3-dimethyl-2,3-bis[2-(4,4-dimethyl-2-oxazolinyl)]butane (**15**) was formed in 26% yield. However, the nitration in system B gave compound **16** in low yield (22%) and none of dimer **15**. The yield of **16** was dramatically increased (83%) when, in an inverse addition, the anion of **14** generated in system B, was added to propyl nitrate in THF (eq 4). The high yield was realized when the temperature of nitration was kept at -40 to -45°. At a temperature of -20 to -25° the yield of **16** was only 10%. At -70 to -78° most of the starting material (60%) was recovered and a small amount of diisopropylnitramine $[(CH_3)_2CH]_2N\text{-}NO_2$ was formed.



14 15 16

(4)

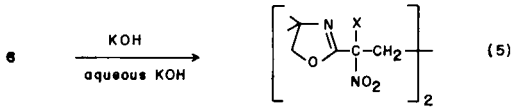
The formation of dimers in the alkyl nitration of tertiary carbanions has been previously noted with 2- and 4-isopropylpyridines [6] and cyclohexylmethylidene-*t*-butylamine [7]. It was established that nitroisopropylpyridines were intermediates in the formation of the 2,3-bis(pyridyl)-2,3-dimethylbutanes and that these dimerizations proceeded

by an electron-transfer process [6]. It is possible, although it has not been verified, that compound **16** was the precursor in the formation of **15**.

Attempts to extend the alkyl nitration to homologs of **14**, such as 2-(2-butyl)-4,4-dimethyl-2-oxazoline, 2-(3-pentyl)-4,4-dimethyl-2-oxazoline and 2-(3-heptyl)-4,4-dimethyl-2-oxazoline were unsuccessful. Generation of *tert*-carbanions with bases such as butyllithium, butyllithium-tetramethylenediamine (TMEDA) and *sec*-butyllithium-TMEDA were fruitless. No deuterium exchange was observed, and no alkylation took place with iodomethane.

The structures of the α-nitroalkyloxazolines were confirmed by spectral data, and by conversion to derivatives such as halonitro compounds.

The halogen derivatives were prepared in high yield by treating aqueous potassium hydroxide solutions of the nitro compounds with potassium hypobromite or hypochlorite. For example, chlorination and bromination of compound **6** afforded 1,4-dichloro- and 1,4-dibromo-1,4-dinitro-1,4-bis[2-(4,4-dimethyl-2-oxazolinyl)]butane in yields of 93% and 95%, respectively (eq 5). In the case of the primary nitro compound **4**, both acidic hydrogens



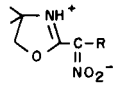
(5)

21, X = Cl
22, X = Br

were replaced by halogens to give 2-(dichloronitromethyl)-and 2-(dibromonitromethyl)-4,4-dimethyl-2-oxazoline in yields of 73% and 93%, respectively.

Spectra of α-Nitroalkyl-2-oxazolines.

The nmr, infrared, and ultraviolet spectra of the primary and secondary α-nitroalkyl-2-oxazolines revealed that the compounds exist mostly in their dipolar structure "A".



"A"

In the nmr spectra a broad singlet, characteristic of the immonium hydrogen was present between 9-10 ppm. There was no indication of the presence of the methine proton in the secondary nitro compounds. In the primary nitro compound **4**, the methine hydrogen appeared as a singlet at 6.57 ppm and the immonium hydrogen at 9.14 ppm.

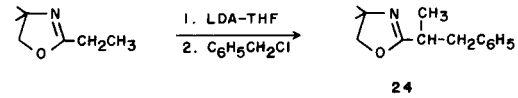
In the infrared spectra, the dipolar structure "A" was confirmed by a strong peak at about 3,300 cm^{-1} characteristic of the immonium group [8]. The nitronate absorptions appeared at 1380-1330 cm^{-1} (asymmetric stretch) and at 1045-1015 cm^{-1} (symmetric stretch) [9].

Corroboration of the dipolar structure was also obtained by ultraviolet spectra which displayed, maxima due to the nitronate function at 324-341 nm.

Preparation of 2-Alkyl-2-oxazolines.

The reaction between the appropriate carboxylic acid and amino alcohol was found to be most suitable for preparing the various oxazolines [10]. However, the procedure was not applicable for synthesizing 2-(diphenylmethyl)-4,4-dimethyl-2-oxazoline (**23**). The high reaction temperature (*ca.* 230°) caused decarboxylation of diphenylacetic acid. Compound **23** was prepared by first reacting diphenylacetyl chloride with 2-amino-2-methylpropanol (AMP) at 0° followed by cyclizing the formed amide in xylene at 170-190° or with thionyl chloride at 0° [11].

In cases in which the required carboxylic acids were not readily available, 2-*sec*-alkyl-2-oxazolines were prepared by alkylating 2-oxazoline derivatives [5d]. This is demonstrated by the preparation of 2-[2-(1-phenylpropyl)-4,4-dimethyl-2-oxazoline (**24**) in 96% yield (eq 6).



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EXPERIMENTAL

Equipment.

All infrared spectra were taken with a Perkin Elmer spectrophotometer, Model 267. Nuclear magnetic resonance spectra were determined on a 90 MHz Model R-32 Perkin Elmer spectrometer using tetramethylsilane as an internal standard. Ultraviolet spectra were obtained on a Cary 17D recording spectrophotometer. Solvents were evaporated on a Buchler flash evaporator.

Apparatus.

Nitrations were performed in a thoroughly dried 500 ml 4-necked flask equipped with a mechanical stirrer, dry ice condenser, thermometer, and pressure equalizing addition funnel. A positive nitrogen pressure was maintained throughout the system.

Materials.

Diisopropylamine and propyl nitrate of Eastman White Label grade were used as received. 2,4,4-Trimethyl-2-oxazoline and 2-ethyl-2-oxazoline from Aldrich were distilled before use. Butyllithium from Alpha Products was titrated before use [12]. THF was purified by a method described in the literature [13].

2-(α-Nitrobenzyl)-4,4-dimethyl-2-oxazoline (**2**).

The following experiment is typical of the procedure employed in the potassium amide-liquid ammonia system (A) [14]. To 300 ml of liquid ammonia at -33° was added a catalytic amount of ferric nitrate and freshly cut potassium metal (4.0 g, 0.10 g-atom). After the potassium amide had formed (5-10 minutes), 2-benzyl-4,4-dimethyl-2-oxazoline [15] (**1**) (9.5 g, 0.05 mole) was added in one portion. The reaction mixture was stirred at -33° for 15 minutes, and propyl nitrate (11.6 g, 0.11 mole) was added as

Table 2

Products From Reactions of 2-Substituted 2-Oxazolines with Alkyl Nitrate

Product [a]	System A [b] Yield % [c]	System B [d] Yield % [c]
2-Nitromethyl-4,4-dimethyl-2-oxazoline (**4**)	13	65 [e,f]
2-Nitroethyl-2-oxazoline (**10**)	72	
2-Nitroethyl-4,4-dimethyl-2-oxazoline (**11**)	88	
2-(1-Nitro-1-pentyl)-4,4-dimethyl-2-oxazoline (**12**)	76	62
2-(**a**-Nitrobenzyl)-4,4-dimethyl-2-oxazoline (**2**)	86	56
2-(1-Nitro-2-cyclohexylethyl)-4,4-dimethyl-2-oxazoline (**8**)	58	67
2-(1-Naphthylnitromethyl)-4,4-dimethyl-2-oxazoline (**13**)	95	
1,4-Dinitro-1,4-bis[2-(4,4-dimethyl-2-oxazoline)]butane (**6**)	55	15
2-(2-Nitro-2-propyl)-4,4-dimethyl-2-oxazoline (**16**)	[g]	22, (83) [h]
2-(Diphenylnitromethyl)-4,4-dimethyl-2-oxazoline (**17**)	47	67, (85)
2-(1-Phenyl-2-nitro-2-propyl)-4,4-dimethyl-2-oxazoline (**18**)	32	43, (77)
2-(1-Phenyl-1-nitropropyl)-4,4-dimethyl-2-oxazoline (**19**)	30	42, (64)
2-[1-(α-Naphthyl)-1-nitropropyl]-4,4-dimethyl-2-oxazoline (**20**)	33	39, (82)

[a] Unless otherwise stated, the primary and secondary nitro compounds were obtained directly after aqueous acidification of their nitronate salts with acetic acid. For the isolation of tertiary nitro compounds see Experimental Section. [b] Potassium amide-liquid ammonia system. [c] Based on starting material. [d] LDA-THF system. [e] Anion formation and nitration were carried out at about -75°. [f] There was also formed, in 5% yield, 1,2-dinitro-1,2-bis[2-(4,4-dimethyl-2-oxazolinyl)]ethane (**9**). [g] The only product isolated was 26% of the dimer 2,3-dimethyl-2,3-bis[2-(4,4-dimethyl-2-oxazolinyl)]butane (**15**). [h] Yield obtained when the anion, generated with LDA-THF at -35° to -40° was added to the alkyl nitrate at -40 to -45° (inverse addition).

fast as possible by keeping the temperature of the reaction mixture below -30 to -40°. (*Caution*: Cooling must be maintained during the addition of the nitrating agent, as long as the vigorous exotherm persists). The nitration mixture was stirred for an additional 30 minutes at -33°, then the ammonia was gradually replaced with absolute ether, and the reaction mixture filtered after room temperature was reached (3-4 hours).

The crude potassium salt (16.17 g) was dissolved in 100 ml of 95% ethanol by warming. Ether (50 ml) was added and on cooling the solution a red oil separated which was decanted. Repeating this procedure gave a clear solution which on cooling afforded the potassium salt of **2** (12.89 g, 94%), mp 296-298° dec; ir (Nujol): 1610 (C=N), 1435 and 1018 cm^{-1} (NO_2^-); nmr (DMSO-d_6): δ 1.24 (s, 6, CH_3), 3.88 (s, 2, CH_2), 6.9-7.26 (m, 3, *m*- and *p*- ring H), and 7.65-7.80 (m, 2, *o*- ring H).

Dissolving the potassium salt (2.72 g, 0.01 mole) in 30 ml of water and acidifying with acetic acid (1.2 g, 0.02 mole) gave the nitro compound **2** (2.08 g, 89%; 84% based on starting material **1**), mp 218-220° (dichloromethane); uv max (ethanol): 340 nm (log ε 4.16); ir (Nujol): 3330 (⁺NH), 1613 (C=N), 1350 and 1028 cm^{-1} (NO_2^-); nmr (deuteriochloroform + DMSO-d_6): δ 1.42 (s, 6, CH_3), 4.28 (s, 2, CH_2), 7.31 (m, 5, ring H), and 10.35 (broad s, 1, ⁺NH); (deuteriochloroform + DMSO-d_6 + deuterium oxide): δ 1.52 (s, 6, CH_3), 4.25 (s, 2, CH_2), 7.36 (m, 5, ring H).

Anal. Calcd. for $C_{12}H_{14}N_2O_3$: C, 61.53; H, 5.98; N, 11.96. Found: C, 61.26; H, 5.98; N, 12.02.

2-(1-Nitroethyl)-2-oxazoline (**10**).

The experimental procedure was similar to that described for the preparation of **2**, except that 2-ethyl-2-oxazoline (4.96 g, 0.05 mole) was used.

The crude potassium salt (1.77 g) was purified by dissolving in warm 95% ethanol and adding a small amount of ether. Cooling gave pure potassium salt (7.43 g, 82%), mp 280-285° dec; ir (Nujol): 1610 (C=N), 1430 and 1075 cm^{-1} (NO_2^-); nmr (deuterium oxide) δ 2.1 (s, 3, CH_3), 3.7-4.0 (t, 2, CH_2), and 4.3-4.55 (t, 2, CH_2).

The potassium salt (1 g, 5.5 mmoles) was dissolved in 5 ml of water and acidified with acetic acid at 0-5°. The mixture was immediately extracted with methylene chloride, the extract dried (magnesium sulfate) and the solvent removed. Washing the residue with hexane gave yellowish-brown 2-(1-nitroethyl)-2-oxazoline (0.7 g, 72% based on starting material), mp 122-123° (benzene); uv max (ethanol): 338 nm (log ε 4.25); ir (Nujol): 3385 (⁺NH); nmr (deuteriochloroform + deuterium oxide) δ 2.1 (s, 3, CH_3), 3.92-4.18 (t, 2, CH_2O), and 4.60-4.91 (t, 2, CH_2) and 9.60 (broad s, 1, ⁺NH).

Anal. Calcd. for $C_5H_8N_2O_3$: C, 41.66; H, 5.55; N, 19.44. Found: C, 41.58; H, 5.72; N, 19.16.

2-(1-Nitroethyl)-4,4-dimethyl-2-oxazoline (**11**).

The general procedure was followed except that 2-ethyl-4,4-dimethyl-2-oxazoline (6.35 g, 0.05 mole) was employed.

The crude potassium salt was found to be unstable in air and was immediately placed in a vacuum desiccator and dried.

The salt (11.5 g) was dissolved in water (50 ml) and acidified at 0-5° with acetic acid to give a yellow solid (6.44 g). The filtrate gave an additional 1.16 g of nitro compound, after extraction with methylene chloride, drying (magnesium sulfate) and removal of solvent. Thus the total yield of 2-(1-nitroethyl)-4,4-dimethyl-2-oxazoline was 7.6 g (88%), mp 162-163° (benzene); uv max (chloroform): 341 nm (log ε 4.34): ir (Nujol): 3320 (⁺NH), 1630 (C=N), 1350 and 1070 cm^{-1} (NO_2^-); nmr (deuteriochloroform): δ 1.51 (s, 6, CH_3), 2.08 (s, 3, CH_3), 4.32 (s, 2, CH_2), and 9.62 (broad s, 1, ⁺NH).

Anal. Calcd. for $C_7H_{12}N_2O_3$: C, 48.83; H, 6.97; N, 16.27. Found: C, 49.00; H, 7.06; N, 16.37.

2-(1-Nitropentyl)-4,4-dimethyl-2-oxazoline (**12**).

The general procedure was used except that 2-pentyl-4,4-dimethyl-2-oxazoline [16] (16.9 g, 0.1 mole) was used.

The crude potassium salt (26.7 g) was acidified with acetic acid to give 2-(1-nitropentyl)-4,4-dimethyl-2-oxazoline (16.18 g 76%), mp 141-141.5° (carbon tetrachloride); ir (Nujol); 3315 (⁺NH), 1630 (C=N), 1355 and 1035 cm^{-1} (NO_2^-); nmr (deuteriochloroform): (200 MHz) δ 0.87-0.94 (t, J = 7.2 Hz, 3, CH_3), 1.22-1.62 (m, 10, $(CH_3)_2$ + $(CH_2)_2CH_3$), 2.48-2.56 (t, J = 7.4 Hz, 2, $CH_2(CH_2)_2CH_3$), 4.32 (s, 2, CH_2O) and 9.60 (broad s, 1, (⁺NH).

Anal. Calcd. for $C_{10}H_{18}N_2O_3$: C, 56.07; H, 8.41; N, 13.08. Found: C, 55.99; H, 8.79; N, 12.89.

2-(1-Naphthylnitromethyl)-4,4-dimethyl-2-oxazoline (**13**).

From 2-(1-naphthylmethyl)-4,4-dimethyl-2-oxazoline (17.93 g, 7.5 mmoles) there was obtained 20.24 g (95%) of the nitro compound, mp 228-229° dec; (dichloromethane); ir (Nujol): 3298 (⁺NH), 1618 (C=N), 1362 and 1045 cm^{-1} (NO_2^-); nmr (deuteriochloroform + DMSO-d_6): (200 MHz) δ 1.52 (s, 6, CH_3), 4.12-4.22 (AB, J = 7.0 Hz, 2, CH_2), 7.44-7.85 (m, 7, ring H), and 10.44 (broad s, ⁺NH).

Anal. Calcd. for $C_{16}H_{16}N_2O_3$: C, 67.60; H, 5.63; N, 9.85. Found: C, 67.80; H, 5.70; N, 9.91.

1,4-Dinitro-1,4-bis[2-(4,4-dimethyl-2-oxazolinyl)]butane (**6**).

From 1,4-bis[2,(4,4-dimethyl-2-oxazolinyl)]butane [17] (**5**) (9.45 g, 0.0375 mole) there was obtained 7.02 g (55%) of **6**, mp 266-267° dec (dimethylformamide); ir (Nujol): 3325 (⁺NH), 1610 (C=N), 1335 and 1015 cm^{-1} (NO_2^-); nmr (DMSO-d_6): δ 1.33 (s, 12, CH_3), 3.30 (s, 4, CH_2), 4.21 (s, 4, CH_2O), and 10.05 (broad s, 2, ⁺NH).

Anal. Calcd. for $C_{14}H_{22}N_4O_6$: C, 49.12; H, 6.48; N, 16.36. Found: C, 49.11; H, 6.77; N, 16.42.

2,3-Dimethyl-2,3-bis[2,(4,4-dimethyl-2-oxazolinyl)]butane (**15**).

The general procedure was followed except that 2-isopropyl-4,4-dimethyl-2-oxazoline (**14**) (10.6 g, 0.075 mole) was used. Replacing ammonia by ether and removing the ether left an orange colored liquid which on distillation at 90-93° (0.5 mm) gave a waxy solid. Sublimation at 0.5 mm gave 2.7 g (26%) of dimer **15**, mp 61-62°; ir (Nujol): 1645 and 1655 cm^{-1} (C=N); nmr (deuteriochloroform): δ 1.29 (s, 24, CH_3) and 3.88 (s, 4, CH_2O).

Anal. Calcd. for $C_{16}H_{28}N_2O_2$: C, 68.53; H, 10.06; N, 9.99. Found: C, 68.18; H, 10.36; N, 9.87.

2-(1-Nitro-2-cyclohexylethyl)-4,4-dimethyl-2-oxazoline (**8**).

The following experiment is typical of the procedure employed in the LDA-THF system (B). Butyllithium (0.065 mole, 28 ml of 2.14 *M* solution of butyllithium in hexane) was added to a solution of diisopropylamine (6.06 g, 0.06 mole) in 75 ml of THF with stirring at 0°. By keeping the temperature below -65°, 2-(2-cyclohexylethyl)-4,4-dimethyl-2-oxazoline (**7**) (0.04 mole, 9.36 g) was added slowly. After stirring for an additional 30 minutes, propyl nitrate (0.06 mole, 6.30 g) was added as fast as possible (6 minutes) by maintaining the temperature at -25 to -30°. The reaction was continued for an additional 30 minutes at the same temperature. After room temperature was attained, THF was removed to give a yellow solid which was dissolved in water. The solution was extracted with methylene chloride and the combined extracts were dried (magnesium sulfate). Removal of solvent left a yellow solid. Additional material was obtained after acidifying the water layer with acetic acid. Washing the combined solids with hexane and recrystallizing with carbon tetrachloride gave 6.80 g (67%) of 2-(1-nitro-2-cyclohexylethyl)-4,4-dimethyl-2-oxazoline, mp 167-168° dec; ir (Nujol): 3315 (⁺NH), 1620 (C=N), 1360 and 1033 cm^{-1} (NO_2^-); nmr (deuteriochloroform): (200 MHz) δ 0.8-1.7 (m, 17, $(CH_3)_2$ + C_6H_{11}), 2.38-2.42 (d, J = 8.0 Hz, 2, CH_2), 4.30 (s, 2, CH_2O), and 9.59 (s, 1, ⁺NH).

Anal. Calcd. for $C_{13}H_{22}N_2O_3$: C, 61.38; H, 8.72; N, 11.01. Found: C, 61.25; H, 9.04; N, 10.96.

2-Nitromethyl-4,4-dimethyl-2-oxazoline (**4**).

The general procedure was followed, except that 0.092 mole of LDA, 0.062 mole of 2,4,4-trimethyl-2-oxazolines (**3**) and 0.092 mole of propyl nitrate were used. Both carbanion generation and nitration were performed at -75°. The reaction mixture was acidified with acetic acid and the resulting solution extracted with methylene chloride. The combined extracts were dried (magnesium sulfate) and the solvent removed to afford 6.32 g (65%) of compound **4**, mp 118-119° dec (benzene); uv max (chloroform): 325 nm (log ε 4.34); ir (Nujol): 3310 (⁺NH), 1639 (C=N), 1380 and 1030 cm^{-1} (NO_2^-); nmr (deuteriochloroform): δ 1.54 (s, 6, CH_3), 4.32 (s, 2, CH_2O), 6.62 (s, 1, CH), and 9.31 (broad s, 1, ⁺NH).

Anal. Calcd. for $C_6H_{10}N_2O_3$: C, 45.56; H, 6.32; N, 17.72. Found: C, 45.67; H, 6.48; N, 17.99.

The benzene insoluble material was recrystallized with methylene chloride to give 0.4 g of 1,2-dinitro-1,2-bis[2-(4,4-dimethyl-2-oxazolinyl)]-ethane (**9**), mp 166-167° dec; ir (Nujol): 3300 (⁺NH), 1626 (C=N), 1385 and 1055 cm^{-1} (NO_2^-); nmr (deuteriochloroform + DMSO-d_6): δ 1.43 (s, 12, CH_3), 4.27 (s, 4, CH_2O), and 10.15 (broad s, 1, ⁺NH); (deuterium oxide) δ 1.40 (s, 12, CH_3) and 4.29 (s, 4, CH_2O).

Anal. Calcd. for $C_{12}H_{18}N_4O_6$: C, 45.85; H, 5.77; N, 17.82. Found: C, 45.74; H, 5.95; N, 17.60.

Compound **9** can be sublimed at 56° and 0.3-0.4 mm.

2-(2-Nitro-2-propyl)-4,4-dimethyl-2-oxazoline (**16**) by Inverse Addition of 4,4-Dimethyl-2-(2-propyl)-2-oxazoline (**14**) Anion to Propyl Nitrate.

The following experiment is typical of the procedure employed. The carbanion of **14** was prepared at 0° from 0.128 mole BuLi, 0.128 mole diisopropylamine and 0.086 mole of **14** dissolved in THF. Then, the carbanion was added *via* a tube, wrapped in glass wool, to a stirred solution of 0.128 mole of propyl nitrate in 50 ml of THF at -40 to -45°. After the addition was complete, the reaction was continued for 30 minutes. Removal of THF gave a brown sticky mass which was dissolved in 100 ml of water and the solution extracted with methylene chloride. Removal of methylene chloride and recrystallization with ethanol gave 13.28 g (83%) of compound **16**, mp 61-61.5°; ir (carbon tetrachloride): 1652 (C=N), 1570 and 1380 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.32 (s, 6, CH_3), 1.85 (s, 6, $(CH_3)_2CNO_2$), and 4.04 (s, 2, CH_2).

Anal. Calcd. for $C_8H_{14}N_2O_3$: C, 51.60; H, 7.58; N, 15.04. Found: C, 51.40; H, 7.81; N, 15.01.

2-Diphenylnitromethyl-4,4-dimethyl-2-oxazoline (**17**).

The experimental procedure was similar to that described for the preparation of **16** except that 2-diphenylmethyl-4,4-dimethyl-2-oxazoline (6.63 g, 0.025 mole) was used. Recrystallization with hexane gave 5.19 g (67%) of compound **17**, mp 75.5-76.5°; ir (Nujol): 1670 (C=N), 1555 and 1380 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.32 (s, 6, CH_3) 4.09 (s, 2, CH_2), and 7.47 (m, 10 ring H).

Anal. Calcd. for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.02. Found: C, 69.62; H, 5.87; N, 8.94.

2-[2-(1-Phenyl-2-nitro)propyl]-4,4-dimethyl-2-oxazoline (**18**).

This compound was obtained in 77% yield, mp 60-61° (chloroform): ir (Nujol): 1675 (C=N), 1560 and 1375 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.25 (s, 6, CH_3), 1.72 (s, 3, H_3C-C), 3.57 (s, 2, CH_2-C_6H_5), 4.02 (s, 2, CH_2O), and 7.25 (m, 5, ring H).

Anal. Calcd. for $C_{14}H_{18}N_2O_3$: C, 64.11; H, 6.92; N, 10.68. Found: C, 63.90; H, 7.00; N, 10.63.

2-[1-(1-Phenyl-1-nitro)propyl]-4,4-dimethyl-2-oxazoline (**19**).

This compound was obtained in 64% yield, mp 64-65° (hexane); ir (Nujol): 1675 (C=N), 1562 and 1377 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 0.99 (t, 3, CH_2CH_3), 1.32 (s, 6, CH_3), 2.74 (q, 2, CH_2CH_3), 4.04 (s, 2, CH_2O), and 7.52 (m, 5, ring H).

Anal. Calcd. for $C_{14}H_{18}N_2O_3$: C, 64.11; H, 6.92; N, 10.68. Found: C, 64.04; H, 6.95; N, 10.73.

2-[1-(α-Naphthyl-1-nitropropyl]-4,4-dimethyl-2-oxazoline (**20**).

This compound was obtained in 82% yield, mp 87-88° (ethanol); ir (Nujol): 1675 (C=N), 1560 and 1375 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 0.98 (t, 3, CH_2CH_3), 1.35 (s, 6, CH_3), 3.01 (q, 2, CH_2CH_3), 4.04 (s, CH_2O), and 7.55-7.97 (m, 7, ring H).

Anal. Calcd. for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.96. Found: C, 68.82; H, 6.50; N, 8.85.

2-(α-Bromo-α-nitrobenzyl)-4,4-dimethyl-2-oxazoline. A. Using the Potassium Salt of 2-(α-Nitrobenzyl)-4,4-dimethyl-2-oxazoline (**2**).

The following experiment is typical of the procedure employed for the bromination of the salts of 2-(α-nitroalkyl)-2-oxazolines. Potassium salt of **2** (1.36 g, 5 mmoles) was dissolved in 10 ml of water, (a pellet of potassium hydroxide was added to obtain a clear solution). To the stirred

solution was added at room temperature a freshly prepared potassium hypobromite solution, obtained from 85% assay potassium hydroxide (1.4 g, 0.025 mole) and bromine (2 g, 0.0125 mole) dissolved in 10 ml of water. The reaction was stirred for 30 minutes, the solid filtered and washed with water to give 1.21 g (77%) of 2-(α-bromo-α-nitrobenzyl)-4,4-dimethyl-2-oxazoline, mp 66° (hexane); ir (Nujol): 1658 (C=N), 1565 and 1334 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.35 (s, 6, CH_3), 4.15 (s, 2, CH_2), 7.35-7.5 (m, 3, ring *m*- and *p*-H), and 7.65-7.78 (m, 2, ring *o*-H).

Anal. Calcd. for $C_{12}H_{13}BrN_2O_3$: C, 46.00; H, 4.15; Br, 25.56; N, 8.94. Found: C, 46.36; H, 4.30; Br, 25.30; N, 9.08.

B. Using Compound **2**.

The following experiment is typical of the procedure employed for the halogenation of 2-(α-nitroalkyl)-2-oxazolines. To a stirred solution of **2** (11.7 g, 0.05 mole) and 85% assay potassium hydroxide (3.96 g, 0.07 mole) in 75 ml of water was added at ambient temperature an aqueous solution of 0.06 mole potassium hypobromite. The mixture was stirred for 30 minutes, and then the precipitate was filtered to give 15.25 g (96%) of 2-(α-bromo-α-nitrobenzyl)-4,4-dimethyl-2-oxazoline, mp 66° (hexane).

2-(α-Chloro-α-nitrobenzyl)-4,4-dimethyl-2-oxazoline.

Method A was followed, except that potassium hypochlorite was used instead of potassium hypobromite. A solution of 1.44 g (5.3 mmoles) potassium salt of **2** in 15 ml of water was added slowly to 20 ml of aqueous potassium hypochlorite (prepared from 3.2 g of 70% calcium hypochlorite (HTH), 2.2 g potassium carbonate and 0.52 g of potassium hydroxide) with stirring at 0-5°. After 30 minutes the precipitate was filtered and washed with water to give 1.27 g (89%) of 2-(α-chloro-α-nitrobenzyl)-4,4-dimethyl-2-oxazoline, mp 58° (hexane); ir (carbon tetrachloride): 1659 (C=N), 1571 and 1330 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.37 (s, 6, CH_3), 4.21 (s, 2, CH_2), 7.45-7.55 (m, 3, ring *m*- and *p*-H), and 7.75-7.87 (m, 2, ring *o*-H).

Anal. Calcd. for $C_{12}H_{13}ClN_2O_3$: C, 53.63; H, 4.84; Cl, 13.22; N, 10.42. Found: C, 53.85; H, 4.87; Cl, 12.98; N, 10.31.

The yield of the chloronitro compound was 99% when Method B was followed.

2-(Dibromonitromethyl)-4,4-dimethyl-2-oxazoline.

The compound was obtained by method B in 90% yield, mp 76° (hexane); ir (carbon tetrachloride): 1658 (C=N), 1585 and 1328 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.35 (s, 6, CH_3), and 4.22 (s, 2, CH_2).

Anal. Calcd. for $C_6H_8Br_2N_2O_3$: C, 22.81; H, 2.55; Br, 50.58; N, 8.87. Found: C, 23.01; H, 2.67; Br, 50.40; N, 9.05.

2-(Dichloronitromethyl)-4,4-dimethyl-2-oxazoline.

The compound was obtained by method B in 75% yield, mp 52° (hexane); ir (carbon tetrachloride): 1670 (C=N), 1600 and 1321 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.40 (s, 6, CH_3), and 4.25 (s, 2, CH_2).

Anal. Calcd. for $C_6H_8Cl_2N_2O_3$: C, 31.74; H, 3.55; Cl, 31.23; N, 12.34. Found: C, 31.86; H, 3.69; Cl, 31.39; N, 12.30.

2-(1-Bromo-1-nitroethyl)-2-oxazoline.

This compound was obtained as a yellow oil by method A in 76% yield, n_D^{20} 1.5065, bp 185-190° at 1.5 mm (Kugelrohr); ir (neat): 1660 (C=N), 1556 and 1440 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 2.52 (s, 3, CH_3), 3.91-4.20 (m, 2, CH_2), and 4.42-4.70 (m, 2, CH_2O).

Anal. Calcd. for $C_5H_7BrN_2O_3$: C, 26.93; H, 3.16; Br, 35.83; N, 12.56. Found: C, 26.94; H, 3.25; Br, 35.71; N, 12.80.

2-(1-Bromo-1-nitroethyl-4,4-dimethyl-2-oxazoline).

This compound was obtained by method B in 96% yield, mp 54-55° (hexane); ir (carbon tetrachloride): 1663 (C=N), 1572 and 1337 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.29 (s, 6, CH_3), 2.45 (s, 3, CH_3), and 4.10 (s, 2, CH_2).

Anal. Calcd. for $C_7H_{11}BrN_2O_3$: C, 33.49; H, 4.42; Br, 31.82; N, 11.16. Found: C, 33.75; H, 4.52; Br, 32.04; N, 11.40.

2-(1-Chloro-1-nitroethyl)-4,4-dimethyl-2-oxazoline.

This compound was obtained by method B in 96% yield, mp 48° (hexane); ir (carbon tetrachloride): 1665 (C=N), 1575 and 1335 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 1.29 (s, 6, CH_3), 2.30 (s, 3, CH_3), and 4.10 (s, 2, CH_2).

Anal. Calcd. for $C_7H_{11}ClN_2O_3$: C, 40.69; H, 5.37; Cl, 17.16; N, 13.56. Found: C, 40.80; H, 5.46; Cl, 17.24; N, 13.80.

2-(1-Bromo-1-nitro-1-pentyl)-4,4-dimethyl-2-oxazoline.

This compound was obtained by method B in 85% yield, bp 115-116° (3.25 mm), n_D^{20} 1.4771; ir (Nujol): 1660 (C=N), 1564 and 1330 cm^{-1} (NO_2); nmr (deuteriochloroform): (200 MHz) δ 0.90-0.97 (t, J = 7 Hz, 3, CH_3), 1.18-1.70 (m, 10, $(CH_3)_2$ + $(CH_2)_2CH_3$), 2.47-2.81 (m, 2, $CH_2(CH_2)_2CH_3$), and 4.06-4.16 (AB, J = 8.1 Hz, 2, CH_2O).

Anal. Calcd. for $C_{10}H_{17}BrN_2O_3$: C, 40.97; H, 5.84; Br, 27.25; N, 9.56. Found: C, 40.81; H, 5.85; Br, 27.25; N, 9.52.

2-(1-Chloro-1-nitro-1-pentyl)-4,4-dimethyl-2-oxazoline.

This compound was obtained by method B in 86% yield, bp 88° (0.9 mm), n_D^{20} 1.4571; ir (Nujol): 1663 (C=N), 1570 and 1330 cm^{-1} (NO_2); nmr (deuteriochloroform): (200 MHz) δ 0.90-0.97 (t, J = 7 Hz, 3, CH_3), 1.15-1.72 (m, 10, $(CH_3)_2$ + $(CH_2)_2CH_3$), 2.44-2.79 (m, 2, $CH_2(CH_2)_2CH_3$), and 4.06-4.15 (AB, J = 8.4 Hz, 2, CH_2O).

Anal. Calcd. for $C_{10}H_{17}ClN_2O_3$: C, 48.29; H, 6.89; Cl, 14.25; N, 11.26. Found: C, 48.57; H, 6.86; Cl, 14.12; N, 11.08.

2-(1-Bromo-1-nitro-2-cyclohexylethyl)-4,4-dimethyl-2-oxazoline.

This compound was obtained by method B in 99% yield, mp 66° (hexane); ir (carbon tetrachloride): 2935 (CH_3), 1664 (C=N), 1570 and 1331 cm^{-1} (NO_2); nmr (deuteriochloroform): (200 MHz) δ 1.15 (m, 6, $(CH_2)_3$), 1.32 (s, 6, CH_3), 1.65 (m, 5, $CH(CH_2)_2$), 2.48-2.74 (dAB, J_{AB} = 15.4 Hz, J_{AX} = 5.8 Hz, J_{BX} = 4.2 Hz, 2, CH_2CBrNO_2), and 4.04-4.15 (AB, J = 8 Hz, 2, CH_2O).

Anal. Calcd. for $C_{13}H_{21}BrN_2O_3$: C, 46.86; H, 6.35; Br, 23.98; N, 8.41. Found: C, 47.05; H, 6.54; Br, 23.77; N, 8.57.

2-(1-Chloro-1-nitro-2-cyclohexylethyl)-4,4-dimethyl-2-oxazoline.

This compound was obtained by method B in 94% yield, mp 66° (hexane); ir (carbon tetrachloride): 2935 (CH_3), 1664 (C=N), 1572 and 1332 cm^{-1} (NO_2); nmr (deuteriochloroform): (200 MHz) δ 1.19 (m, 6, $(CH_2)_3$), 1.33 (s, 6, CH_3); 1.64 (m, 5, $CH(CH_2)_2$), 2.44-2.73 (dAB, J_{AB} = 15.25 Hz, J_{AX} = 5.9 Hz, J_{BX} = 4.5 Hz, 2, CH_2CClNO_2, and 4.04-4.14 (AB, J = 8.5 Hz, 2, CH_2O).

Anal. Calcd. for $C_{13}H_{21}ClN_2O_3$: C, 54.07; H, 7.83; Cl, 12.28; N, 9.70. Found: C, 53.80; H, 7.36; Cl, 12.10; N, 9.62.

2-(1-Naphthylbromonitromethyl)-4,4-dimethyl-2-oxazoline.

This compound was obtained by method B in 100% yield, mp 183-184° dec (chloroform); ir (Nujol): 1653 (C=N), 1565 and 1365 cm^{-1} (NO_2); nmr (DMSO-d_6): (200 MHz) δ 1.44 (s, 6, CH_3) 4.12-4.25 (AB, J = 8.7 Hz, 2, CH_2), and 7.51-7.93 (m, 7, ring H).

Anal. Calcd. for $C_{16}H_{15}BrN_2O_3$: C, 52.91; H, 4.16; Br, 22.00; N, 7.71. Found: C, 53.00; H, 4.07; Br, 21.97; N, 7.51.

2-(1-Naphthylchloronitromethyl)-4,4-dimethyl-2-oxazoline.

This compound was obtained by method B in 98% yield, mp 182-183° dec (chloroform); ir (Nujol): 1660 (C=N), 1560 and 1370 cm^{-1} (NO_2); nmr (DMSO-d_6): (200 MHz) δ 1.31 (s, 6, CH_3), 4.33-4.47 (AB, J = 8.6 Hz, 2, CH_2), and 7.62-8.07 (m, 7, ring H).

Anal. Calcd. for $C_{16}H_{15}ClN_2O_3$: C, 60.29; H, 4.74; Cl, 11.12; N, 8.79. Found: C, 60.06; H, 4.72; Cl, 11.28; N, 8.57.

1,4-Dibromo-1,4-dinitro-1,4-bis[2-(4,4-dimethyl-2-oxazolinyl)]butane (**22**).

This compound was obtained by method B in 92% yield, mp 202-203° dec (chloroform); ir (Nujol): 1665 (C=N), 1580 and 1335 cm^{-1} (NO_2); nmr (chloroform): (200 MHz) δ 1.32 (s, 6, CH_3), 2.68-3.11 (m, 4, CH_2), and 4.07-4.17 (AB, J = 8.6 Hz, 2, CH_2O).

Anal. Calcd. for $C_{14}H_{20}Br_2N_4O_6$: C, 33.62; H, 4.03; Br, 31.95; N, 11.20. Found: C, 33.59, H, 4.13; Br, 31.85; N, 11.11.

1,4-Dichloro-1,4-dinitro-1,4-bis[2-(4,4-dimethyl-2-oxazolinyl)]butane (**21**).

This compound was obtained by method B in 93% yield, mp 189-190° dec (carbon tetrachloride); ir (Nujol): 1670 (C=N), 1583 and 1338 cm^{-1} (NO_2); nmr (deuteriochloroform): (200 MHz) δ 1.33 (s, 6, CH_3), 2.62-3.08 (m, 4, CH_2) and 4.15-4.07 (AB, J = 8.7 Hz, 4, CH_2O).

Anal. Calcd. for $C_{14}H_{20}Cl_2N_4O_6$: C, 40.89; H, 4.90; Cl, 17.24; N, 13.62. Found: C, 40.87; H, 4.95; Cl, 17.22; N, 13.49.

2-(1-Naphthylmethyl)-4,4-dimethyl-2-oxazoline.

The following experiment is typical for the preparation of 2-substituted-2-oxazolines. α-Naphthylacetic acid (32.25 g, 0.173 mole) was added to 2-amino-2-methylpropanol (AMP) (23.09 g, 0.259 mole). The formed salt was heated slowly and the resulting liquid was refluxed 4 hours by keeping the bath temperature at about 230°. When the vapor temperature had dropped from 176° to 156°, water formed in the reaction was removed at 105° *via* a 12" vigreux column provided with a downward condenser. Then excess AMP was removed at 103° (18 mm) and the residue was distilled at 148-150° (0.7-1 mm) to give 38.15 g (92%) of 2-(1-naphthylmethyl)-4,4-dimethyl-2-oxazoline, mp 56-57°; ir (Nujol): 1662 cm^{-1} (C=N); nmr (deuteriochloroform): δ 1.22 (s, 6, CH_3), 3.82 (s, 2, CH_2), 4.02 (s, 2, CH_2O), and 7.35-8.25 (m, 7, ring H).

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.20; N, 5.83. Found: C, 80.53; H, 7.24; N, 5.83.

2-(2-Cyclohexylethyl)-4,4-dimethyl-2-oxazoline.

From 78.13 g (0.5 mole) of 3-cyclohexylpropanoic acid and 66.76 g (0.75 mole) of AMP there was obtained 78.39 g (75%) of the oxazoline, bp 96° (0.8 mm), n_D^{20} 1.4642; ir (neat): 1663 cm^{-1} (C=N); nmr (deuteriochloroform): δ 0.70-1.80 (m, 19, $(CH_3)_2$ + $CH_2C_6H_{11}$), 2.14-2.31 (t, J = 7.65 Hz, 2, CH_2), and 3.88 (s, 2, CH_2O).

Anal. Calcd. for $C_{13}H_{23}NO$: C, 74.59; H, 11.08; N, 6.69. Found: C, 74.23; H, 11.46; N, 7.06.

2-Pentyl-4,4-dimethyl-2-oxazoline [16].

This compound was prepared in 60% yield, bp 98° (26 mm), n_D^{20} 1.4316; ir (neat): 1669 cm^{-1} (C=N); nmr (deuteriochloroform): (200 MHz) δ 0.86-0.93 (t, J = 6.5 Hz, 3, CH_3), 1.26 (s, 6, CH_3), 1.30-1.35 (m, 4, $(CH_2)_2CH_3$), 1.55-1.70 (pentet, J = 7.4 Hz, 2, $CH_2(CH_2)_2$), 2.20-2.27 (t, J = 7.6 Hz, 2, $CH_2(CH_2)_3CH_3$), and 3.89 (s, 2, CH_2O).

2-Isopropyl-4,4-dimethyl-2-oxazoline (**14**).

The usual procedure was followed. However, since **14** co-distilled with the water formed in the reaction, the distillate was extracted with methylene chloride. Drying the combined extracts (magnesium sulfate) and removing the solvent gave 80% of compound **14**, bp 135-136°; ir (neat): 1665 cm^{-1} (C=N); nmr (deuteriochloroform): δ 1.15 (d, 6, $(CH_3)_2CH$), 1.23 (s, 6, CH_3), 2.57 (m, 1, CH), and 3.85 (s, 2, CH_2O).

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C, 67.83; H, 11.10; N, 9.92.

2-(Diphenylmethyl)-4,4-dimethyl-2-oxazoline (**23**).

Diphenylacetyl chloride (23.05 g, 0.1 mole) dissolved in 30 ml of methylene chloride was added dropwise to AMP (17.83 g, 0.2 mole) in 220 ml of methylene chloride at 0° with stirring. After an additional hour at 0°, the reaction mixture was allowed to stand overnight at ambient temperature. The solution was washed with water to remove any unreacted AMP and then was dried (magnesium sulfate). Removal of solvent gave *N*-[2-(1-hydroxy-2-methyl)propyl]diphenylacetamide in 44 g (88%) yield, mp 165.5-166°; ir (Nujol): 3282 and 3103 (NH), 1665 cm^{-1} (CO); nmr (deuteriochloroform): δ 1.22 (s, 6, CH_3), 3.55 (s, 2, CH_2O), 4.30 (s, 1, OH), 4.88 (s, 1, CH), 5.85 (s, 1, NH), and 7.29 (s, 10, ring H).

The amide was cyclized without further purification to **23**.

Using Thionyl Chloride.

Thionyl chloride (4.76 g, 0.04 mole) was added dropwise with stirring at 0° to 2.83 g (0.01 mole) of the amide dissolved in 40 ml of methylene chloride. The reaction was continued for 2 hours more at 0° and then the solution was added slowly to 550 ml of 2*M* sodium hydroxide at 0°. The lower layer was washed with water, dried (magnesium sulfate) and then evaporated. The residue, which was distilled at 138-139° (0.5 mm) solidified on standing. Recrystallization with hexane gave 2.21 g (83%) of compound **23**, mp 57-58°; ir (Nujol): 1650 cm^{-1} (C=N); nmr (deuteriochloroform): δ 1.21 (s, 6, CH_3), 3.88 (s, 2, CH_2), 5.06 (s, 1, CH), and 7.24 (m, 10, ring H).

Anal. Calcd. for $C_{18}H_{19}NO$: C, 81.46; H, 7.23; N, 5.28. Found: C, 81.12; H, 7.22; N, 5.18.

Using Thermal Cyclization.

The amide was heated in xylene at 170-190° for 20 hours. Then water was removed azeotropically with xylene and the residue distilled to give 2.31 g (87%) of **23**.

2-(1-Phenyl-2-propyl)-4,4-dimethyl-2-oxazoline (**24**).

The following experiment is typical of the alkylation procedure employed. All operations were carried out under nitrogen. Butyllithium (9.2 ml, 0.022 mole) was added at 0° with stirring to 2.23 g (0.022 mole) of diisopropylamine dissolved in THF. After 10 minutes, the reaction mixture was cooled below -70° and 2-ethyl-4,4-dimethyloxazoline (2.54 g, 0.02 mole) was added slowly. The reaction was continued for an additional 30 minutes and then benzyl chloride (3.04 g, 0.024 mole) dissolved in 20 ml of THF was added by keeping the temperature below -70°. The reaction was continued for 30 minutes and then was allowed to attain ambient temperature. Removal of THF and distillation of the residue afforded 4.18 g (96%) of compound **24**, bp 110-110.5° (4 mm), n_D^{20} 1.4996; nmr (deuteriochloroform): δ 1.15 (d, 9, CH_3), 2.78 (d, 2, CH_2), 3.03 (m, 1, CH), and 3.85 (s, 2, CH_2O).

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.36; H, 8.83; N, 6.45. Found: C, 77.08; H, 9.03; N, 6.48.

2-(1-Phenyl-1-propyl)-4,4-dimethyl-2-oxazoline.

Compound **1** (21.55 g, 0.114 mole) and bromoethane (38.46 g, 0.353 mole) gave 20.7 g (84%) of 2-(1-phenyl-1-propyl)-4,4-dimethyl-2-oxazoline, bp 103-104° (4 mm), n_D^{20} 1.5027; nmr (deuteriochloroform): δ 0.88 (t, 3, CH_2CH_3), 1.21 (s, 6, CH_3), 1.85 (m, 2, CH_2), 3.41 (t, 1, CH), 3.79 (s, 2, CH_2O), and 7.24 (m, 5, ring H).

Anal. Calcd. for $C_{14}H_{19}NO$: C, 77.36; H, 8.83; N, 6.45. Found: C, 76.96; H, 8.99; N, 6.59.

2-(2-Butyl)-4,4-dimethyl-2-oxazoline.

2-Ethyl-4,4-dimethyl-2-oxazoline (14.9 g, 0.12 mole) and bromoethane (20.92 g, 0.192 mole) gave 12.95 g (70%) of product, bp 148-150°, n_D^{20} 1.4290; nmr (deuteriochloroform): δ 0.92 (t, 3, CH_2CH_3), 1.15 (d, 3, $CHCH_3$), 1.27 (s, 6, CH_3), 1.62 (m, 2, CH_2), 2.37 (m, 1, CH), and 3.92 (s, 2, CH_2O).

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.03; N, 9.02. Found: C, 69.31; H, 11.39; N, 8.95.

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