# Facile and Convenient Synthesis of 2,6-Disubstituted 4*H*-1,3-Oxazin-4-one Derivatives



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Facile and convenient methods for the preparation of a variety of 2,6-disubstituted 4*H*-1,3-oxazin-4-ones **3** by three complementary methods are described. Treatment of the branched aliphatic imidate **2c,d** with diketene **1** in the presence of a catalytic amount of acetic acid affords 2-substituted 6-methyl-1,3-oxazin-4-ones **3c,d**, whereas the unbranched imidate **2b,e** gave oxazines **3b,e** and pyrimidines **4b,e** (Method A). The reaction of acyl Meldrum's acid **5** with imidate **2** afford 2,6-disubstituted oxazine **3**, though the alkylimidate with acetyl Meldrum's acid yielded **3** and 5-acetyl-1,3-oxazine-4,6-dione **8** (Method B). The cylodehydration of acylacetylcarboxamide **13** with acid, such as 70% perchloric acid or fluorosulfonic acid, afforded 1,3-oxazines **3** (Method C).

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## Introduction.

4*H*-1,3-Oxazin-4-ones are useful precursors and building blocks for the synthesis of poly-functionalized nitrogen containing heterocyclic compounds [1]. A number of methods for the synthesis of these oxazines have been reported [1]. These methods include the [4+2] cycloaddition reaction of 1,4-dipolar compounds, such as the diketene or acylketene generated by the thermolysis of 2,3-dihydrofuran-2,3-dione or 1,3-dioxin-4-one derivatives to the carbon-carbon triple bond of acetylene derivatives or carbon-nitrogen triple bond of cyanate or cyanamide.

This paper describes facile and convenient methods for the synthesis of oxazines by the [4+2] cycloaddition reaction of diketene or acyl Meldrum's acid (5-acyl-2,2-dimethyl-1,3-dioxane-4,6-dione) to imidates, or the cyclodehydration of *N*-acylacetylcarboxamides.

## Results and Discussion.

### I. Reaction of Diketene with Aliphatic Imidate (Method A).

Previously, Kato *et al.* [2] reported the cycloaddition reaction of diketene to the carbon-nitrogen double bond of the imidate to give 2-substituted 2-ethoxy-6-methyl-3,4-dihydro-2*H*-1,3-oxazin-4-one derivatives. The treatment of these dihydrooxazines, bearing an aromatic substituent at the 2-position on the oxazine ring, with a catalytic amount of acetic acid afforded 4*H*-1,3-oxazin-4-ones with the loss of ethanol. In contrast, the treatment of these dihydrooxazines, bearing an aliphatic substituent at the 2-position on the oxazine ring with acid yielded ring-opened acetoacetylcarboxamide, whereas heating of the dihydrooxazines afforded 5-acetyl-2,6-disubstituted 4(3*H*)-pyrimidones.

It was found that the reaction of aliphatic imidate **2b-e** with diketene **1** in benzene or tetrahydrofuran (THF) in the presence of a catalytic amount of acetic acid gave 4*H*-1,3-oxazin-4-ones and in some cases together with pyrimidones **4**. Imidates used in this reaction are ethyl propionimidate (**2b**), ethyl isobutyrimidate (**2c**), methyl trimethylacetimidate (**2d**), and ethyl phenylacetimidate (**2e**).

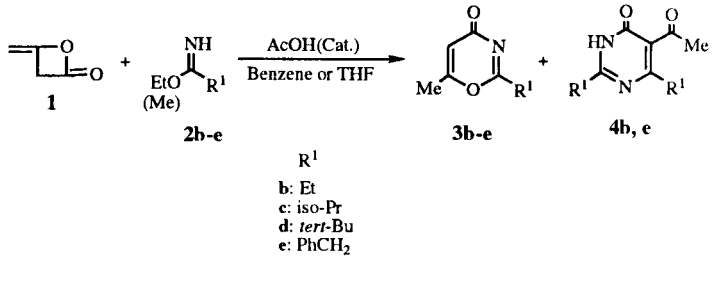
Thus, imidate **2b** and two equivalents of diketene was allowed to react in benzene with a catalytic amount of acetic acid under reflux to give the corresponding oxazine **3b** and pyrimidone **4b** in 52% and 32% yield, respectively. The use of THF as a solvent instead of benzene slightly improved the yield of oxazine (see Table I). Similarly, imidate **2e** reacted with **1** in THF to give oxazine **3e** and pyrimidine **4e** in 27% and 53% yield, respectively.

On the other hand, an imidate bearing a branched alkyl group, such as isopropyl **2c** or *tert*-butyl **2d**, reacted with **1** in benzene to give oxazine **3c**, **3d** as the sole product in 84% yield in each case.

The structures of these oxazines **3b-e** were determined on the basis of the analytical and spectral chracteristics (see Experimental).

### II. Reaction of Acyl Meldrum's Acid with Imidate (Method B).

Scheme 1



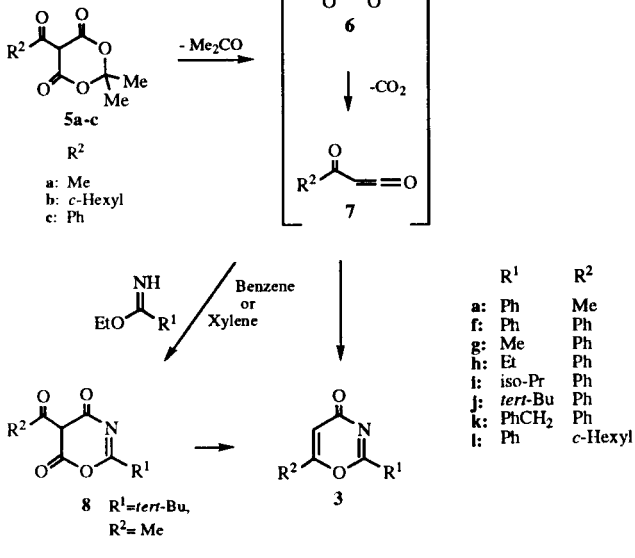

Acyl Meldrum's acids have been widely utilized as a precursor of acylketene. In a previous paper [3] from this laboratory, it has been reported that the reaction of acyl Meldrum's acid with Schiff bases afforded 5-acyl-1,3-oxazine-4,6-dione derivatives as the major product together with a trace of 2,3,6-trisubstituted 2,3-dihydro-1,3-oxazin-4-one-5-carboxylic acids. We considered that the reaction of acyl Meldrum's acid with imidate would open a new route for the synthesis of 4*H*-1,3-oxazin-4-one derivatives.

When ethyl benzimidate (**2a**) was allowed to react with two equivalents of acetyl Meldrum's acid (**5a**) in benzene under reflux, 6-methyl-2-phenyl-4*H*-1,3-oxazin-4-one (**3a**) was obtained in 75% yield together with ethyl acetoacetate. The structure of **3a** was confirmed by the comparison of its infrared (ir) spectrum with the authentic sample [2a]. Furthermore, the reaction of benzimidate with cyclohexanecarbonyl Meldrum's acid (**5b**) afforded the 6-cyclohexyl-2-phenyl-4*H*-1,3-oxazin-4-one (**3l**) in 71% yield. Similarly, benzoyl Meldrum's acid (**5c**) reacted with several aliphatic or benzimidate to give the corresponding 2-substituted 6-phenyl-1,3-oxazines **3f-k** in moderate to good yields.

On the other hand, the reaction of imidate **2d** with **5a** in benzene under reflux gave 5-acetyl-1,3-oxazine-4,6-dione derivative **8** in nearly quantitative yield. The direct treatment of **2d** with **5a** in xylene resulted in the formation of an inseparable mixture **8** and **3d** with compound **8** predominating. The diones **8** were unexpectedly stable and upon heating in xylene for 12 hours, **8** were quantitatively recovered. The structures were determined on the basis of the analytical and spectral characteristics (see Experimental).

The formation of **8** and **3** can be rationalized by the intermediates **6** and **7** indicated in Scheme 2.

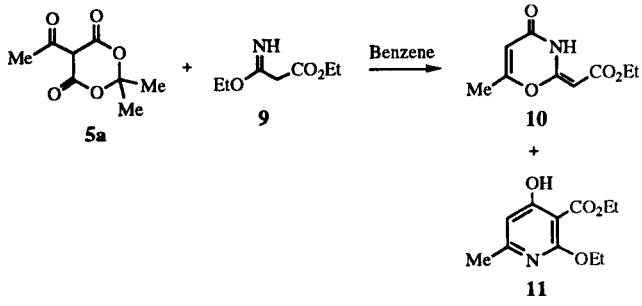
Scheme 2




Furthermore, this method was applied to the synthesis of 2-ethoxycarbonylmethylene-3,4-dihydro-6-methyl-2*H*-1,3-oxazin-4-one (**10**), which was previously prepared by the reaction of diketene with ethyl 1-ethoxyformimidoylacetate (**9**) in 17% yield [4].

Teatment of **9** with acetyl Meldrum's acid (**5a**) in benzene at reflux afforded **10** in 80% yield together with a trace of pyridine derivative **11** (Scheme 3).

Scheme 3

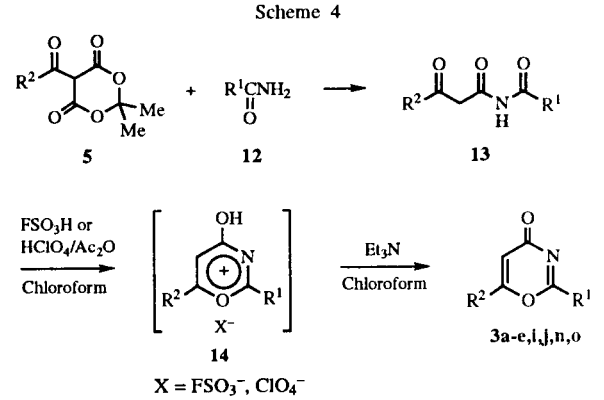



III. Cyclodehydration of *N*-Acylacetylcarboxamides (Method C).

We have previously reported [5] the formation of 1,3-oxazinium salts from *N*-acylacetylcarboxamide with various acids such as 70% perchloric acid, 98% sulfuric acid, 36% hydrochloric acid, saturated hydrogen chloride-ethanol, trifluoroacetic acid, and acetic acid. Among these acids, 70% perchloric acid was most effective for the formation of the 1,3-oxazinium salts. The synthesis of 4*H*-1,3-oxazin-4-ones *via* the oxazinium salts from a variety of *N*-acylacetylcarboxamides was investigated.

The treatment of the 1,3-oxazimium salt **14** ($R^1$ = Ph, $R^2$ = Me), which was prepared from *N*-acetoacetylbenzamide (**13a**) with 70% perchloric acid and acetic anhydride, with triethylamine afforded 6-methyl-2-phenyl-4*H*-1,3-oxazin-4-one (**3a**) in 73% yield. Fluorosulfonic acid was found to be more effective as an acid than perchloric acid in this method. Thus, the simple treatment of *N*-acetoacetylbenzamide with fluorosulfonic acid followed by neutralization with triethylamine in the same flask yielded **3a** in 75% yield. Similarly, 2-substituted 6-methyl- **3b-e** and 2-substituted 6-phenyl-1,3-oxazin-4-one **3i,j,n** were prepared using this method (Scheme 4).

Scheme 4




Conclusion.

In conclusion, a wide variety of 2,6-disubstituted 4*H*-1,3-oxazin-4-one derivatives can be prepared through

three complementary methods, A, B, and C. Substituents and the yield of the oxazines prepared by these methods are shown in Table I.

Method A is convenient for the large scale preparation of 2-alkyl-6-methyl derivatives. Method B is convenient for the preparation of oxazines bearing several substituents at the 2- and 6-positions of the oxazine ring, though there are certain restrictions. Method C is more applicable because of the greater availability of amides over imidate.

Table I

Preparation of 2,6-Disubstituted 4*H*-1,3-Oxazin-4-ones **3a-o**.

| No. | $R^1$ | $R^2$ | Method A [a] Yield (%) | Method B Yield (%) | Method C Yield (%) (Acid) |
|---|---|---|---|---|---|
| **a** | Ph | Me | -- | 75 | 73 ($HClO_4$) 75 ($FSO_3H$) |
| **b** | Et | Me | 52 (32) [b] 64 (24) [c] | -- | 70 ($HClO_4$) |
| **c** | iso-Pr | Me | 84 | | 59 ($FSO_3H$) |
| **d** | *tert*-Bu | Me | 84 | -- | 61 ($FSO_3H$) |
| **e** | $PhCH_2$ | Me | 27 (53) [c] | -- | 78 ($FSO_3H$) |
| **f** | Ph | Ph | -- | 89 | -- |
| **g** | Me | Ph | -- | 74 | -- |
| **h** | Et | Ph | -- | 72 | -- |
| **i** | iso-Pr | Ph | -- | 70 | 65 ($FSO_3H$) |
| **j** | *tert*-Bu | Ph | -- | 68 | 60 ($FSO_3H$) |
| **k** | $PhCH_2$ | Ph | -- | 67 | -- |
| **l** | Ph | *c*-Hexyl [d] | -- | 71 | -- |
| **m** | $EtO_2CCH_2$ | Me | -- | 80 | -- |
| **n** | MeCH=CH | Ph | -- | -- | 70 ($HClO_4$) |
| **o** | PhCH=CH | Me | -- | -- | 89 ($HClO_4$) |

[a] The yields of the pyrimidine derivatives are shown in parentheses. [b] In benzene. [c] In tetrahydrofuran. [d] *c*-Hexyl = cyclohexyl.

## EXPERIMENTAL

Melting points were determined on a Mel-Temp melting point apparatus using an open capillary tube. All melting and boiling points are uncorrected. The ir spectra were taken on a Perkin Elmer 1600 FT-IR spectrophotometer. The nmr spectra were measured on a JEOL JNM-PMX 60 instrument. Deuteriochloroform was used as the solvent for all substances. Chemical shifts are reported in δ values downfield relative to the internal standard tetramethylsilane. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Mass spectra were obtained using a Hitachi RMU-6MG spectrometer. Microanalyses were performed on a Perkin Elmer elemental analyzer type 2400 CHN. Tetrahydrofuran was distilled from lithium aluminum hydride. Chloroform was dried over anhydrous calcium chloride and distilled from phosphorus pentoxide before use. Triethylamine distilled from calcium hydride.

Method A.

2-Ethyl-6-methyl-4*H*-1,3-oxazin-4-one (**3b**) and 2,6-Diethyl-5-acetyl-4(3*H*)-pyrimidone (**4b**).

In Benzene.

A solution of ethyl propylimidate (**2b**) (0.505 g, 5 mmoles), diketene (**1**) (0.84 g, 10 mmoles), and few drops of acetic acid in dry benzene (5 ml) was heated at reflux for 12 hours. The solvent was evaporated *in vacuo* to give an oil. Fractional vacuum distillation of the oil gave **3a** in 52% yield. The residue of the distillation solidified upon cooling, which was recrystallized from hexane gave 32% of **4b**. The ir spectrum of this compound was identical with the authentic sample prepared by literature procedure [2b].

2-Ethyl-6-methyl-4*H*-1,3-oxazin-4-one (**3b**).

This compound was obtained as colorless oil, bp 85-87°/0.4 Torr; ir (neat): ν CO 1672 $cm^{-1}$; $^1H$ nmr : 1.33 (t, 3H, $CH_3$, J = 7 Hz), 2.26 (s, 3H, 6-$CH_3$), 2.70 (q, 2H, $CH_2$, J = 7 Hz), 6.03 (s, 1H, 5-H); ms: m/z 139 ($M^+$).

*Anal.* Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.57; H, 6.64; N, 10.34.

In Tetrahydrofuran.

A solution of ethyl propylimidate (**2b**) (1.01 g, 10 mmoles), diketene (**1**) (1.68 g, 20 mmoles), and few drops of acetic acid in tetrahydrofuran (10 ml) was heated at reflux for 24 hours. After work-up as described for benzene refluxing, **3b** and **4b** were obtained in 64% and 24% yield, respectively.

6-Methyl-2-isopropyl-4*H*-1,3-oxazin-4-one (**3c**).

A solution of methyl isopropylimidate (**2c**) (2.02 g, 20 mmoles), diketene (**1**) (3.53 g, 42 mmoles), and few drops of acetic acid in dry benzene (20 ml) was heated at reflux for 15 hours. The solvent was evaporated *in vacuo* to give an oil. Fractional vacuum distillation of the oil gave **3c** (84 %), bp 99-100°/0.9 Torr; ir (neat) : ν CO 1670 $cm^{-1}$; $^1H$ nmr: 1.31 (d, 6H, isopropyl, J = 7 Hz), 2.34 (s, 3H, 6-$CH_3$), 2.60-3.10 (m, 1H, CH), 5.97 (s, 1H, 5-H); ms: m/z 153($M^+$).

*Anal.* Calcd. for $C_8H_{11}NO_2$ : C, 62.73 ; H, 7.24 ; N, 9.14. Found : C, 62.67 : H, 7.44 ; N, 9.08.

2-*tert*-Butyl-6-methyl-4*H*-1,3-oxazin-4-one (**3d**).

A solution of methyl *tert*-butylimidate (**2d**) (2.30 g, 20 mmoles), diketene (**1**) (3.53 g, 42 mmoles), and few drops of acetic acid in dry benzene (20 ml) was heated at reflux for 15 hours. The solvent was evaporated *in vacuo* to give an oil. Fractional vacuum distillation of the oil gave **3d** (84 %), bp 79-81°/ 0.1 Torr; ir (neat): ν CO 1668 $cm^{-1}$; $^1H$ nmr : 1.33 (s, 9H, *tert*-butyl), 2.24 (s, 3H, 6-$CH_3$), 5.96 (s, 1H, 5-H); ms: m/z 167 ($M^+$).

*Anal.* Calcd. for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.53; H, 7.76; N, 8.14.

2-Benzyl-6-methyl-4*H*-1,3-oxazin-4-one (**3e**) and 5-Acetyl-2,6-dibenzyl-4 (3*H*)-pyrimidone (**4e**).

A solution of ethyl benzylimidate (**2e**) (3.26 g, 20 mmoles), diketene (**1**) (3.36 g, 40 mmoles), and few drops of acetic acid in tetrahydrofuran (20 ml) was heated at reflux for 24 hours. The solvent was evaporated to give semisolid. Dry ether was added to the residue. Ether insoluble solid was filtered off and recrystallized from methanol gave **4e** in 53% yield. The ir spectrum was identical with the authentic sample prepared by literature procedure [2a]. The filtrate was evaporated and resulting liquid was distilled under vacuum to give **3e** in 27% yield.

2-Benzyl-6-methyl-4*H*-1,3-oxazin-4-one (**3e**).

This compound was obtained as colorless oil, bp 145°/0.4 Torr; ir (neat): ν CO 1668 $cm^{-1}$; $^1H$ nmr: 2.14 (s, 3H, 6-$CH_3$), 3.90 (s, 2H, $CH_2$), 5.94 (s, 1H, 5-H), 7.23 (s, 5H, phenyl); hrms: 201.0791 ($M^+$, Calcd. for $C_{12}H_{11}NO_2$ : 201.0789 ).

Method B.

General Procedure for the Reaction of Acyl Meldrum's Acids **5** with Imidates (**2**).

A suspension of acyl Meldrum's acid **5** (10 mmoles) and imidate (**2**) (5 mmoles) in 10 ml of benzene was heated at reflux for 30 minutes with stirring. After evaporation of the solvent, dry ether was added to the residual semisolid. Ether insoluble solid was filtered off. Evaporation of the filtrate, followed by distillation off ethyl acetoacetate or ethyl benzoylacetate, to give small amount of solid. The combined solid was purified by recrystallization to give oxazine **3f-l**.

2,6-Diphenyl-4*H*-1,3-oxazin-4-one (**3f**).

This compound was obtained as colorless prisms (benzene), mp 160-161°; ir (potassium bromide): ν CO 1670 $cm^{-1}$; $^1H$ nmr: 6.61 (s, 1H, 5-H); ms: m/z 249 ($M^+$).

*Anal.* Calcd. for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 76.93; H, 4.30; N, 5.60.

2-Methyl-6-phenyl-4*H*-1,3-oxazin-4-one (**3g**).

This compound was obtained as colorless needles (ether), mp 137-139°; ir (potassium bromide): ν CO 1676 $cm^{-1}$; $^1H$ nmr: 2.53 (s, 3H, $CH_3$), 6.56 (s, 1H, 5-H), 7.33-7.86 (m, 5H, phenyl); ms : m/z 187 ($M^+$).

*Anal.* Calcd. for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.69; H, 5.02; N, 7.30.

2-Ethyl-6-phenyl-4*H*-1,3-oxazin-4-one (**3h**).

This compound was obtained as colorless needles (ether/benzene), mp 115-117°; ir (potassium bromide): ν CO 1670 $cm^{-1}$; $^1H$ nmr: 1.40 (t, 3H, $CH_3$, J = 7 Hz), 2.83 (q, 2H, $CH_2$, J = 7 Hz), 6.60 (s, 1H, 5-H), 7.43-7.90 (m, 5H, phenyl); ms : m/z 201 ($M^+$).

*Anal.* Calcd. for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.72; H, 5.45; N, 6.88.

6-Phenyl-2-isopropyl-4*H*-1,3-oxazin-4-one (**3i**).

This compound was obtained as colorless needles (ether), mp 109-110°; ir (potassium bromide): ν CO 1671 $cm^{-1}$; $^1H$ nmr: 1.43 (d, 6H, isopropyl, J = 7 Hz), 2.81-3.28 (m, 1H, CH), 6.58 (s, 1H, 5-H), 7.43-7.91 (m, 5H, phenyl); ms: m/z 215 ($M^+$).

*Anal.* Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.49; H, 6.10; N, 6.30.

2-*tert*-Butyl-6-phenyl-4*H*-1,3-oxazin-4-one (**3j**).

This compound was obtained as colorless prisms (ether), mp 139-140°; ir (potassium bromide): ν CO 1670 $cm^{-1}$; $^1H$ nmr: 1.46 (s, 9H, *tert*-Bu), 6.56 (s, 1H, 5-H), 7.34-7.90 (m, 5H, phenyl); ms: m/z 229 ($M^+$).

*Anal.* Calcd. for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.34; H, 6.58; N, 6.06.

2-Benzyl-6-phenyl-4*H*-1,3-oxazin-4-one (**3k**).

This compound was obtained as colorless needles (ether/benzene), mp 137-138°; ir (potassium bromide): ν CO 1667 $cm^{-1}$; $^1H$ nmr: 4.03 (s, 2H, $CH_2$), 6.53 (s, 1H, 5-H), 7.30-7.76 (m, 10H, phenyl); ms: m/z 263 ($M^+$).

*Anal.* Calcd. for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.26; H, 5.25; N, 5.16.

6-cyclo-Hexyl-2-phenyl-4*H*-1,3-oxazin-4-one (**3l**).

This compound was obtained as colorless needles (ether), mp 105-106°; ir (potassium bromide): ν CO 1681 $cm^{-1}$; $^1H$ nmr: 1.06-2.73 (m, 11H, cyclohexyl), 6.05 (s, 1H, 5-H), 7.40-8.30 (m, 5H, phenyl); ms: m/z 255 ($M^+$).

*Anal.* Calcd. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.33; H, 6.62; N, 5.53.

5-Acetyl-2-*tert*-butyl-5,6-dihydro-4*H*-1,3-oxazine-4,6-dione (**8**).

To a solution of methyl *tert*-butylimidate (**2d**) (0.23 g, 2 mmoles) in dry benzene (5 ml) was added acetyl Meldrum's acid (**5a**) (0.744 g, 4 mmoles), and the mixture was heated at reflux for 14 hours. The solvent was evaporated *in vacuo* to give an oily residue, which was distilled under vacuum to give 0.38 g, bp 95-100° (bath temperature)/1 Torr; ir (neat): ν CO 1723, 1687 $cm^{-1}$; $^1H$ nmr: 1.36 (s, 9H, *tert*-Bu), 2.70 (s, 3H, $COCH_3$), 17.13 (br, 1H, enol OH); ms m/z 211 ($M^+$).

*Anal.* Calcd. for $C_{10}H_{13}NO_4$: C, 56.87: H, 6.20; N,6.63. Found: C, 56.81; H, 6.50; N, 6.93.

6-Methyl-2-*tert*-butyl-4*H*-1,3-oxazin-4-one (**3d**) and 5-Acetyl-2-*tert*-butyl-5,6-dihydro-4*H*-1,3-oxazine-4,6-dione (**8**).

To a solution of methyl *tert*-butylimidate (**2d**) (1.29 g, 10 mmoles) in dry xylene (20 ml), was added acetyl Meldrum's acid (**5a**) (3.72 g, 20 mmoles) and the mixture was heated at reflux for 3 hours. The solvent was evaporated *in vacuo* to give an oily residue. Vacuum distillation of the oil gave a mixture (1.53 g) of **3d** and **8** (3.5:1), which was analyzed by nmr and glc.

2-Ethoxycarbonylmethylene-3,4-dihydo-6-methyl-2*H*-1,3-oxazin-4-one (**11**) and Ethyl 2-ethoxy-4-hydroxy-6-methylpyridine-3-carboxylate (**12**).

A solution of ethyl 1-ethoxyformimidoylacetate (**9**) (0.795 g, 5 mmoles) and acetyl Meldrum's acid (**5a**) (1.86 g, 10 mmoles) in dry benzene (10 ml) was heated at reflux for 1 hour. The solvent was evaporated *in vacuo* to give an oily residue. The residue was separated by silica gel column chromatography (ethyl acetate-hexane 1:1, v/v) to give **10** in 80% yield and trace of **11**. These compounds **10** and **11** were identical in every respect with the authentic samples prepared by literature procedure [4].

Method C.

General Procedure by the Use of Fluorosulfonic Acid.

To an ice-salt cooled solution of *N*-acylacetylcarboxamide **13** (10 mmoles) in freshly distilled chloroform (100 ml), fluorosulfonic acid (3 g, 30 mmoles) was added dropwise for a period of few minutes under nitrogen atmosphere. After completion of the addition cooling bath was removed, and reaction mixture was stirred for a period of 4 hours at room temperature. Triethylamine (9.09 g, 90 mmoles) was added dropwise over a period of 30 minutes to the reaction mixture in an ice-salt cooled bath. Then chloroform solution was washed with water (20 ml x 3) and dried over anhydrous sodium sulfate. After evaporation of the solvent, crude product was purified by vacuum distillation or recrystallization.

General Procedure by the Use of 70% Perchloric Acid.

To a solution of *N*-acylacetylcarboxamide **13** (10 mmoles) in freshly distilled chloroform (15 ml), acetic anhydride (5.1 g, 50 mmoles) and 70% perchloric acid (1.43 g, 10 mmoles) was added successively in an ice-cooled bath with stirring. The reaction mixture was stirred for 1 additional hour. Anhydrous ether (80 ml) was added to the reaction mixture. Precipitated 1,3-oxazinium salt **14** was filtered off and dried under vacuum. To a suspension of **14** in benzene (30 ml), equimolar amount of triethylamine was added and stirred for 5 more minutes. The benzene solution was washed with water (10 ml x 3) and dried over anhydrous sodium sulfate. After evaporation of the solvent, crude product was purified by vacuum distillation or recrystallization.

2-Crotyl-6-methyl-4*H*-1,3-oxazin-4-one (**3n**).

This compound was obtained as colorless prisms (ether), mp 96-97°; ir (potassium bromide): 1690 $cm^{-1}$; $^1H$ nmr: 1.93 (dd, 3H, J =2, 7 Hz), 2.24 (s, 3H, 6-$CH_3$), 5.90 (s, 1H, 5-H), 5.80-6.30 (m, 1H), 6.80-7.50 (m, 1H); ms: m/z 151 ($M^+$).

*Anal.* Calcd. for $C_8H_9NO_2$: C, 63.53; H, 6.00; N, 9.27. Found: C, 63.63; H, 6.09; N, 9.06.

2-Styryl-6-methyl-4*H*-1,3-oxazin-4-one (**3o**).

This compound was obtained as colorless prisms (benzene), mp 153-155°; ir (potassium bromide): 1670 $cm^{-1}$; $^1H$ nmr: 2.24 (s, 3H, 6-$CH_3$), 5.93 (s, 1H, 5-H), 6.57 (d, 1H, J = 16 Hz), 7.20-7.53 (m, 5H, phenyl), 7.88 (d, 1H, J = 16 Hz); ms: m/z 213 ($M^+$).

*Anal.* Calcd. for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.05; H, 5.14; N, 6.51.

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REFERENCES AND NOTES

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