Anal. Calcd for $C_{12}H_6N_2O$: C, 74.22; H, 3.14. Found: C, 74.30; H, 3.12.

***N*-Methyl-7-cyanobenzofuro[3,2-*b*]pyridinium Iodide (16).** 7-Cyanobenzofuro[3,2-*b*]pyridine (0.097 g) and methyl iodide (0.213 g) were dissolved in benzene (30 mL) and heated in a Fischer-Porter tube at 100 °C for 3 days. The yellow crystals were filtered (0.165 g, 98%) and recrystallized from methanol (15 mL) to give yellow needles of *N*-methyl-7-cyanobenzofuro[3,2-*b*]-pyridinium iodide (0.147 g, 85.7%): mp 285–287 °C dec; IR (KBr) 2242 cm^{-1} (C≡N); ^1H NMR (CF_3COOH) δ 9.2–8.1 (m, 6 H), 5.03 (s, 3 H, CH_3); mass spectrum, *m/e* 194 ($M^{+\cdot} - CH_3I$).

Anal. Calcd for $C_{13}H_9IN_2O$: C, 46.43; H, 2.68. Found: C, 46.29; H, 2.74.

Acknowledgment. We thank the National Institutes of Health (GM 25242) for support of this work. The cooperative work with Poland was supported by NSF and Fundusz Marri Skłodowskiej–Curie Grant 01P-75-020490. We also thank Reilly Tar and Chemical Corp. for the gift of some pyridine 1-oxides.

Registry No. **5** (X = Me; R = NO_2), 69593-46-0; **5** (X = Cl; R = NO_2), 84499-14-9; **5** (X = Br; R = NO_2), 69593-44-8; **5** (X = Br; R = CN), 84499-16-1; **5** (X = Br; R = 3,5-$(NO_2)_2$), 84499-18-3; **5** (X = I; R = NO_2), 84499-20-7; **5** (X = OMe; R = NO_2), 84499-22-9; **5** (X = CO_2Me; R = NO_2), 63801-86-5; **5** (X = CO_2Me; R = CN), 84499-24-1; **5** (X = COMe; R = NO_2), 84499-26-3; **6** (X = Cl; R = NO_2), 84499-27-4; **6** (X = Br; R = NO_2), 83702-39-0; **6** (X = Br; R = CN), 84499-28-5; **6** (X = Br; R = 4,6-$(NO_2)_2$), 84520-42-3; **6** (X = I; R = NO_2), 84499-29-6; **6** (X = I; R = NO_2) acetate, 84499-30-9; **6** (X = OMe; R = NO_2), 84499-31-0; **6** (X = H; R = NO_2), 33400-82-7; **6** (X = H; R = NO_2) acetate, 84499-32-1; **7** (X = Me; R = NO_2), 84499-33-2; **7** (X = Br; R = NO_2), 84499-34-3; **8a**, 84499-35-4; **8b**, 84499-36-5; **9**, 84499-37-6; **10**, 67274-82-2; **11**, 84499-38-7; **12**, 54499-49-9; **12** picrate, 84499-39-8; **13**, 244-80-4; **13** picrate, 84558-13-4; **14**, 76167-49-2; **15**, 84499-40-1; **16**, 84499-41-2; 2,2,6,6-tetramethylpyridine, 768-66-1; *p*-nitrobenzenediazonium tetrafluoroborate, 456-27-9; *p*-cyanobenzenediazonium tetrafluoroborate, 2252-32-6; potassium phenoxide, 100-67-4; 3-hydroxypyridine, 109-00-2; *o*-bromonitrobenzene, 577-19-5; benzofuro[3,2-*b*]pyridine-7-diazonium cation, 84499-42-3; 3-(*o*-nitrophenoxy)pyridine, 76167-50-5; 3-(*o*-nitrophenoxy)-pyridine picrate, 84499-43-4; potassium 3-bromo-2-(5-cyano-2-hydroxyphenyl)pyridine, 84499-44-5.

Aza Cope Rearrangements in the Cyclopropenyl- and Allyl-Substituted Δ^2-Oxazolinone Systems

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Received August 10, 1982

The scope of the thermal and photochemical reorganization reactions of a number of cyclopropenyl- and allyl-substituted oxazolinones has been examined. These systems undergo a facile sigmatropic rearrangement in accord with orbital symmetry predictions. 2-Methyl-4-allyl-Δ^2-oxazolinones were found to undergo a 3,3 sigmatropic allyl shift on thermolysis to give the Δ^3-oxazolinone isomer. In contrast, on direct irradiation the 2-methyl-4-allyl-Δ^3-oxazolinones undergo a 1,3 allyl shift to give the Δ^2 isomer. The 4,4-disubstituted Δ^2-oxazolinones undergo decarbonylation either on irradiation or by flash vacuum pyrolysis to give acetimides. The acetimides formed were easily hydrolyzed to give the corresponding ketones. The excited-state behavior of the 2-phenyl-4-methyl-Δ^2-oxazolinone system was found to be markedly different from that encountered with the 2-methyl-4-phenyl-substituted isomer. The rationale for the difference in behavior is discussed.

Together with nitrile imines, oxides, sulfides and selenides, nitrile ylides belong to a class of 1,3-dipoles to which the general name nitrilium betaines has been given.[1] These reactive species have been known for over 20 years[2] and continue to elicit the interest of both experimental[3] and theoretical chemists.[4] 1,3-Dipolar cycloaddition of this class of 1,3-dipoles has led to the synthesis of a variety of interesting heterocyclic compounds.[5,6] Recently, it has been shown that 1,1 intramolecular cycloaddition of nitrile ylides can compete with the normal 1,3-addition when certain geometric constraints are imposed.[7,8] In these cases, the reactions have been formulated in terms of the carbene form of the dipole.[4,8] Beside the Huisgen procedure which involves the elimination of hydrogen chloride from imidoyl chlorides,[9] other accesses to nitrile ylides include (a) elimination of phosphoric acid ester from 2,3-dihydro-1,4-Δ^5-oxazaphospholes,[10] (b) photolysis of 2*H*-azirines,[5,6] and (c) thermal elimination of carbon dioxide from oxazolinones.[11] The thermolysis of trisubstituted Δ^3-oxazolinones (**1**) has been studied in some detail by Steglich and co-workers.[11–16] These compounds readily lose carbon dioxide at moderate temperatures and form products expected from nitrile ylides. If the dipole contains groups capable of conjugation, 1,5-dipolar electrocyclization is observed.[13] When alkyl groups are present on the nitrile ylide carbon centers, the dipole can be trapped with various dipolarophiles.[14–16]

† John Simon Guggenheim Memorial Fellow, 1981–1982.

(1) Huisgen, R.; Grashey, R.; Sauer, J. "The Chemistry of Alkenes"; Patai, S., Ed., Interscience: London, 1964; p 739.
(2) Huisgen, R.; Stangl, H.; Sturm, H. J.; Wagenhofer, H. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 50.
(3) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565.
(4) Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 6397. Caramella, P.; Gandour, R. W.; Hall, J. A.; Deville, C. G.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 385.
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(12) Steglich, W. *Fortschr. Chem. Forsch.* **1969**, *12*, 77.
(13) Hofle, G.; Steglich, W. *Chem. Ber.* **1971**, *104*, 1408.

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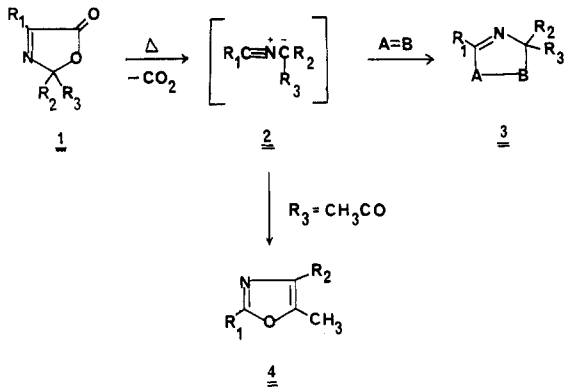
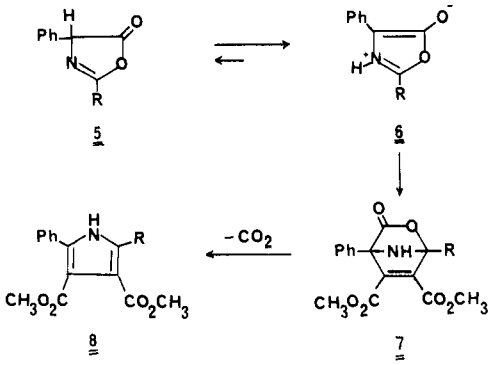
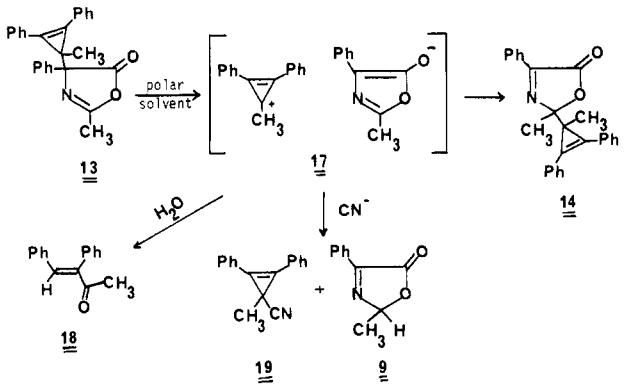


As a rule, Δ^3-oxazolinones lose carbon dioxide more readily than the Δ^2 isomers. Attempted thermolysis of 2,4,4-trisubstituted Δ^2-oxazolinones in refluxing xylene is reported to cause no reaction.[17] In the case of 2,4-disubstituted Δ^2-oxazolinones **5**, it has been observed that in the presence of dipolarophiles, such as dimethyl acetylenedicarboxylate, the loss of carbon dioxide follows second-order kinetics.[17] From this observation it was concluded that nitrile ylides do not intervene as intermediates in these cycloadditions. Instead, the tautomeric form **6** of the azlactone system undergoes the cycloaddition reaction with subsequent extrusion of carbon dioxide.



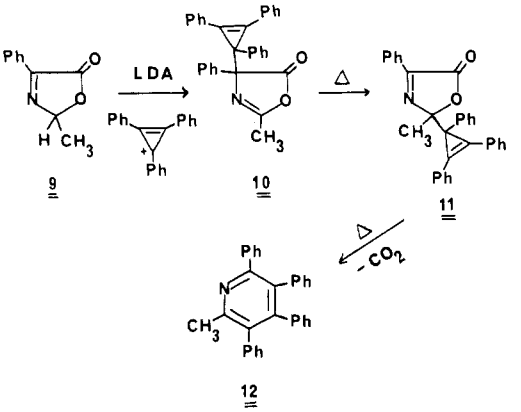
Higher temperatures and proper substituents allow the thermolysis of trisubstituted Δ^2-oxazolinones to give carbon dioxide loss and products expected from nitrile ylide intermediates.[18] Elimination of carbon monoxide to give an enamide has also been observed, but only when a 2-trifluoromethyl[19] and a 4-thiophenoxy group[20] are present in a 2,4,4-trisubstituted Δ^2-oxazolinone. Because of the theoretical and experimental challenge of nitrile ylide cycloaddition, we have studied the thermal and photochemical behavior of several allyl-substituted oxazolinones in the hope of obtaining additional examples of 1,1-cycloaddition.[21] We have found that these allyl-substituted oxazolinones undergo a facile sigmatropic rearrangement prior to carbon dioxide extrusion.[22] In this paper we report the results of these studies.

Scheme I



Results and Discussion

As part of a research program concerned with small-ring heterocyclic compounds, we initiated a study dealing with the thermolysis of several 3-cyclopropenyl-substituted oxazolinones as a method for synthesizing azabenzvalene derivatives.[23] Heating a sample of Δ^2-oxazolinone **10**, derived by treating azlactone **9** with LDA and triphenylcyclopropenyl perchlorate, at 55 °C for 90 min gave rise to Δ^3-oxazolinone **11**. Further heating of **11** produced 2-methyl-3,4,5,6-tetraphenylpyridine (**12**), mp 160–161 °C, in high yield.[24]



In order to help elucidate the mechanism involved in the thermal reorganization of **10** to **11**, we decided to investigate a number of related systems especially since there are very few reports of Cope rearrangements involving cyclopropene moieties.[25] Heating Δ^2-oxazolinone **13** at 80 °C for 90 min produced the Δ^3-isomer **14** in quantitative yield. Interestingly, reorganization of the unsymmetrical cyclopropenyl-substituted Δ^2-oxazolinone **15** to the symmetrical isomer **16** was observed when **15** was heated at 130 °C.

The rate of reorganization of the Δ^2 isomer (e.g., **10**) to the Δ^3 isomer (e.g., **11**) was found to be markedly dependent on the polarity of the solvent employed. The rearrangement was extremely sluggish when performed in cyclohexane or benzene but proceeded much more rapidly in a polar solvent such as acetonitrile. The solvent dependence upon the rate of reaction favors an ionic mechanism for the rearrangement of the Δ^2 to the Δ^3 isomer. A very reasonable pathway involves heterolytic cleavage of the cyclopropene–oxazolinone bond to give a tight ion

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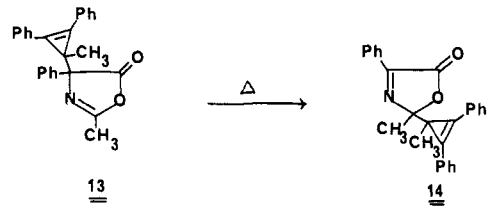
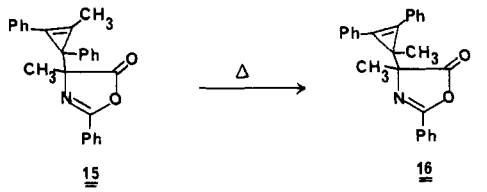
(21) Engel, N.; Fischer, J.; Steglich, W. *J. Chem. Res.* **1977**, 162.
(22) For a preliminary report, see Padwa, A.; Akiba, M.; Cohem, L. A.; MacDonald, J. G. *Tetrahedron Lett.* **1981**, 2435.
(23) Padwa, A.; Akiba, M.; Cohen, L. A.; Gingrich, H. L.; Kamigata, N. *J. Am. Chem. Soc.* **1982**, *104*, 286.
(24) The mechanism associated with the conversion of 11 to 12 will be addressed in a future publication.
(25) For some leading references, see Padwa, A.; Blacklock, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2797.



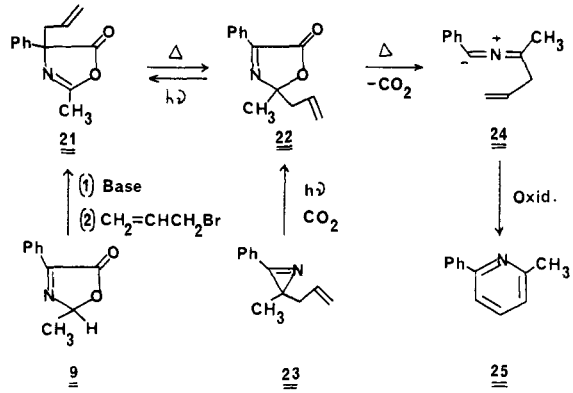
13 14



15 16

pair that subsequently collapses to the products. The driving force for this reaction involves the creation of a more highly conjugated π system in the Δ^3 isomer. In addition, a smaller steric interaction between the phenyl and methyl groups exists and probably also plays a role in controlling the direction of reaction (e.g., **15** → **16**). Support for this mechanism comes from carrying out the thermolysis of **13** in the presence of potassium cyanide (Scheme I). Under these conditions the yield of **14** is substantially diminished and 3-cyanocyclopropene **19** and azlactone **9** were also isolated. Heating an acetonitrile solution of **13** in the presence of water produced enone **18** as well as azlactone **9**. All of this is consistent with the trapping of ion-pair **17**. It should be pointed out that other examples of allylic migrations of cyclopropenes that proceed through a dissociation–reassociation path are known in the literature and provide good analogy for the pathway outlined above.[26]

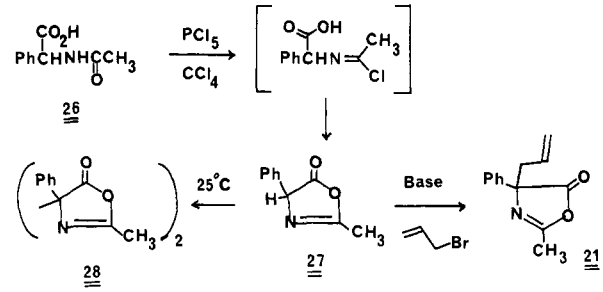
Although the rearrangements encountered with the cyclopropenyl-substituted oxazolinones can be accommodated by the mechanism outlined in Scheme I, several other plausible routes involving a series of 3,3 sigmatropic shifts were considered as likely alternatives. To aid in distinguishing among these pathways, we have examined the thermal and photochemical behavior of a number of allyl-substituted oxazolinones. 4-Allyl-substituted 2-methyl-4-phenyl-Δ^2-oxazolin-5-ones were prepared by treating oxazolinone **9** with an allylic halide in the presence of Hunig's base according to the general procedure of Steglich.[27] Heating a sample of Δ^2-oxazolinone **21** in



9 23 25

benzene at 135 °C resulted in the formation of the rearranged Δ^3-isomer **22** (98% yield). This material was identified by comparison with an independently synthesized sample prepared from the irradiation of azirine **23** in the presence of carbon dioxide. Previous work by Padwa and Schmid had shown that nitrile ylides generated from the photolysis of 2*H*-azirines could be readily trapped by carbon dioxide to give Δ^3-oxazolinones in high yield.[28,29] On further heating, oxazolinone **22** was converted to 2-methyl-6-phenylpyridine (**25**). The formation of **25** can be postulated to arise by an initial extrusion of carbon dioxide to give nitrile ylide **24**, which undergoes internal reorganization followed by a subsequent oxidation. In contrast to the thermal results, the photolysis of **22** produced Δ^2-oxazolinone **21** in quantitative yield. The conversion of **22** to **21** is probably related to the fact that **22** possesses a much larger extinction coefficient and is preferentially converted to **21** with Pyrex filtered light.

At this stage of our studies we decided to develop an alternate synthesis of Δ^2-oxazolinone (**9**) that would be more practical than the one currently used that involves irradiation of 2-phenyl-3-methylazirine in the presence of carbon dioxide. Our intention was to generate oxazolinone **9** under relatively mild conditions and at ambient temperatures. To achieve this goal, *N*-acetylphenylglycine (**26**) and a slight excess of phosphorus pentachloride was stirred in carbon tetrachloride at 25 °C for 5 h. The major compound isolated was assigned as 2-methyl-4-phenyl-Δ^2-oxazolinone (**27**) on the basis of its spectral properties. This



26 28 27 21

species was extremely labile and rapidly dimerized to give two new compounds. One of these was assigned as dimer **28**, but the other compound was too labile to be fully characterized. The dimers obtained are quite different from those reported by Schmid and co-workers.[18] The anion derived from **27** could be alkylated with allyl bromide to give **21**. Unfortunately, the yield associated with the alkylation was very low and further work with this system was abandoned.

In order to determine whether the sigmatropic rearrangement of oxazolinones **21** and **22** was of 1,3 or 3,3 character, the allyl moiety was replaced by a 3-methyl-2-butenyl group. This was accomplished by treating **9** with 1-bromo-3-methyl-2-butene and a catalytic amount of potassium iodide in dimethylformamide at 90 °C. Thermolysis of Δ^2-oxazolinone **29** in benzene at 162 °C gave the Δ^3-isomer **30**. The formation of the 1,1-dimethyl-2-propenyl-substituted oxazolinone is only compatible with the 3,3 sigmatropic rearrangement route. In contrast, the direct irradiation of Δ^3-oxazolinone **31** gave exclusively the 4-(3-methyl-2-butenyl)-substituted Δ^2-oxazolinone **29**. Oxazolinone **31** was prepared by trapping the nitrile ylide derived from azirine **32** with carbon dioxide. The structure of **29** was unambiguously established by comparison with an independently synthesized sample. The above results indicate that the photoinduced rearrangement of the Δ^3-oxazolinone system proceeds via a 1,3 sigmatropic shift

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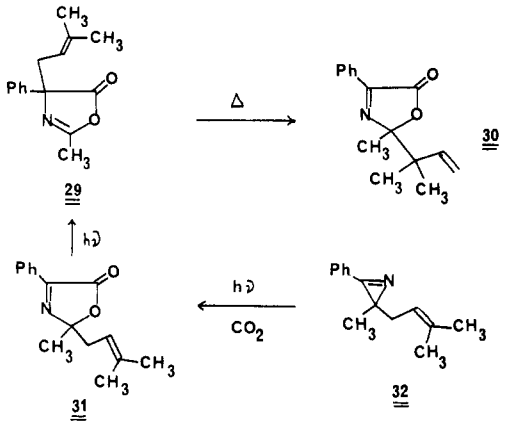
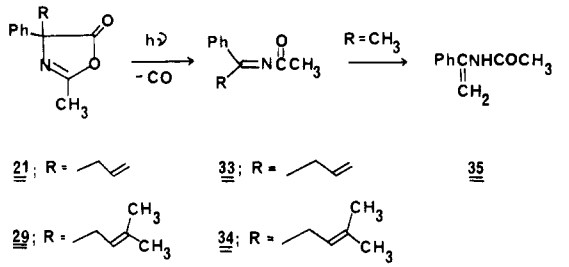
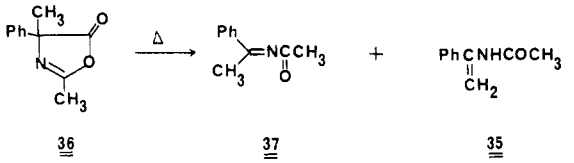


of the allyl moiety. Thus, the sigmatropic nature of the above rearrangements is perfectly consistent with orbital symmetry predictions.[30]

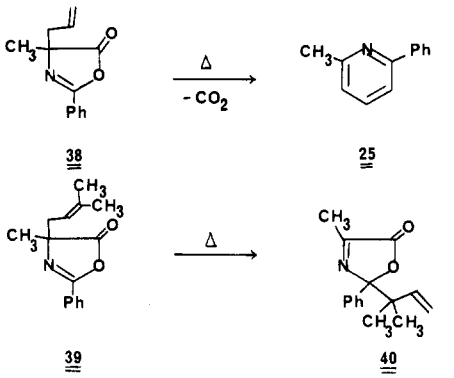
It should also be pointed out that on prolonged irradiation, Δ^2-oxazolinones **21** and **29** were found to undergo decarbonylation to give acetimides **33** and **34**, which were



easily hydrolyzed to the corresponding ketones. Additional examples of this type of photodecarbonylation were provided by the photolysis of a series of Δ^2-oxazolinones (R = CH_3, C_2H_5), $PhCH_2$). In all of these cases, hydrolysis of the acetimides gave the expected ketones. As additional evidence, the acetimide derived from 2,4-dimethyl-4-phenyl-Δ^2-oxazolinone was found to undergo base-induced tautomerization to yield enamide **35**. This material was independently prepared from the reaction off benzonitrile, methylmagnesium bromide, and acetyl chloride. The light-induced expulsion of carbon monoxide from a 2,4,4-trisubstituted Δ^2-oxazolinone as observed with compounds **21** and **29** has ample precedent in the literature.[19,31] Carbon monoxide may also be lost from the Δ^2-oxazolinone system under thermal conditions.[32,33] In our case, the flash vacuum pyrolysis of oxazolinone **36** produced a mixture of compounds **35** and **37**.

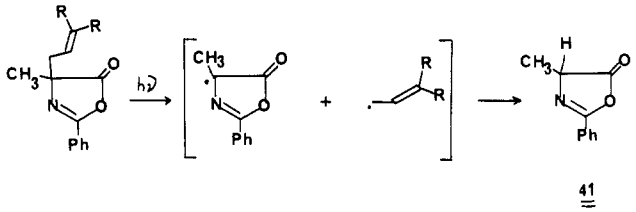


Attention was next turned to the excited state and thermal behavior of the closely related 2-phenyl-4,4-disubstituted Δ^2-oxazolinone system. 4-Allyl- (**38**) and 4-(3-methyl-2-butenyl)-2-phenyl-4-methyl-Δ^2-oxazolinones (**39**) were prepared according to the method of Steglich and co-workers.[27] Thermolysis of **38** produced 2-methyl-6-phenylpyridine (**25**) as the major product. We believe that



the formation of **25** from **38** involves initial extrusion of carbon dioxide and formation of a transient nitrile ylide intermediate that is subsequently converted to the observed product. There is a good possibility that **38** initially isomerizes to give the Δ^3 isomer which undergoes a subsequent loss of carbon dioxide. In fact, thermolysis of **39** afforded the Cope rearranged product **40** when heated at 150 °C, thereby providing good evidence for the above suggestion.

We have also found that the excited-state behavior of the 2-phenyl-4-methyl-substituted Δ^2-oxazolinone system (i.e., **38** and **39**) is markedly different from the closely related 2-methyl-4-phenyl-substituted isomer (i.e., **21** or **29**). While irradiation of the latter system readily results in the loss of carbon monoxide, oxazolinones **38** and **39** are stable to irradiation. Extended photolysis eventually induced cleavage of the allylic C–C bond to generate a pair of radicals that ultimately produce oxazolinone **41**. One



possible explanation for the photostability of compounds **38** and **39** toward decarbonylation is that scission of the carbonyl group in the Norrish type I sense is less likely to occur when a methyl group is present on the 4-position of the Δ^2-oxazolinone ring. When a phenyl group is adjacent to the carbonyl functionality, α cleavage to give a diradical followed by loss of carbon monoxide will occur to give the observed acetimide. This path is somewhat related to that postulated for the photo-Fries reaction.[34,35]

One final point worth discussing involves a comparison of the chemical behavior of the Δ^2- and Δ^3-oxazolinones. As a rule, Δ^3-oxazolinones lose carbon dioxide and give nitrile ylides more readily than the Δ^2 isomers. The latter compounds give nitrile ylides only when rupture of the O_1–C_2 bond is favored with respect to cleavage of the C_4–C_5 bond. Usually, 2-oxazolinones lose carbon monoxide in a cheletropic type of reaction more readily than expulsion of carbon dioxide in a cycloelimination reaction. Our results indicate that 4-allylated 2-oxazolinones suffer a 2-aza Cope rearrangement and give the corresponding 2-allylated 3-oxazolinones prior to the expulsion of either carbon monoxide or carbon dioxide.

(30) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.
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Experimental Section[36]

Preparation of 2-Methyl-4-phenyl-Δ^3-oxazolinone (9). A solution containing 4.0 g of 2-phenyl-3-methylazirine in 400 mL of benzene was saturated with carbon dioxide.[28] The solution was irradiated for 4.5 h with a 450-W Hanovia lamp equipped with a Corex filter sleeve. During the irradiation, carbon dioxide was continually bubbled through the solution. Removal of the solvent under reduced pressure left a brown residue, which was chromatographed on a silica gel column using benzene as the eluent. Removal of the solvent under reduced pressure afforded 2.84 g (54%) of a yellow oil which was distilled at 80–90 °C (1 mm) to give a colorless oil whose structure was assigned as 2-methyl-4-phenyl-Δ^3-oxazolin-5-one (**9**) on the basis of the following data: NMR ($CDCl_3$, 60 MHz) δ 1.54 (d, 3 H, J = 6.0 Hz), 5.96 (q, 1 H, J = 6.0 Hz), 7.05–7.92 (m, 3 H), 8.12–8.49 (m, 2 H); IR (neat) 1775, 1610, 1485, 1445, 1365, 1310, 1295, 1140, 1060, 990, 980, 920, 800, 740, 680 cm^{-1}.

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.52; H, 5.32; N, 7.80.

Preparation of 2-Phenyl-4-methyl-Δ^2-oxazolinone (41). A solution containing 13.5 g of *N*-benzoyl-*dl*-alanine and 35 mL of acetic anhydride was heated at 80 °C under a nitrogen atmosphere for 20 min. The excess acetic anhydride was removed under reduced pressure and the residue was distilled at 135 °C (0.3 mm) to give 9.23 g (75%) of a clear colorless oil whose structure was identified as 2-phenyl-4-methyl-Δ^2-oxazolinone (**41**) on the basis of the following spectral data: NMR ($CDCl_3$, 60 MHz) δ 1.47 (d, 3 H, J = 6.5 Hz), 4.31 (q, 3 H, J = 6.5 Hz), 7.26–8.03 (m, 5 H); IR (neat) 1840, 1670, 1460, 1330, 1300, 1270, 1170, 1120, 1060, 1010, 920, 890, 790, 700 cm^{-1}.

Anal. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.47; H, 5.17; N, 7.98.

Preparation of 2-Methyl-4-phenyl-4-(1,2,3-triphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (10). To a solution containing 1.9 mL of diisopropylamine in 32 mL of tetrahydrofuran was added 8.9 mL of a 1.4 M *n*-butyllithium solution at 0 °C. The mixture was allowed to stir at 0 °C for 15 min and then a solution containing 2.10 g of 2-methyl-4-phenyl-Δ^3-oxazolin-5-one in 32 mL of tetrahydrofuran was added to the LDA solution at 0 °C. After stirring at 0 °C for 2 h, the reaction mixture was added to a stirred suspension containing 4.40 g of triphenylcyclopropenyl perchlorate[37] in 100 mL of tetrahydrofuran at −78 °C. After stirring at −78 °C for 3 h, the reaction mixture was allowed to stir for an additional 4 h at room temperature. The solution was quenched with water and the organic layer was concentrated under reduced pressure. The residue was taken up in ether and washed with water. The ether layer was dried and concentrated under reduced pressure to give 4.2 g of a crude oil, which was subjected to flash chromatography with benzene as the eluent. The first material isolated from the column contained 780 mg (15%) of a yellow solid which was recrystallized from acetone–hexane to give 2-methyl-4-phenyl-4-(1,2,3-triphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (**10**) as a white solid: mp 131–132 °C; IR (KBr) 1800, 1684, 1493, 1445, 1380, 1241, 1135, 902, 745, 682 cm^{-1}; UV (cyclohexane) 299, 238, 305, 319, 337 nm (ϵ 27 000, 21 900, 17 700, 25 900, 20600); NMR ($CDCl_3$, 60 MHz) δ 2.06 (s, 3 H), 6.92–8.23 (m, 15 H); ms, m/e 441, 397, 320, 267.

Anal. Calcd for $C_{31}H_{23}NO$: C, 84.33; H, 5.25; N, 3.17. Found: C, 84.25; H, 5.28; N, 3.14.

Thermal Rearrangement of 2-Methyl-4-phenyl-4-(1,2,3-triphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (10). A solution containing 150 mg of Δ^2-oxazolinone **10** in 1.0 mL of acetonitrile was heated at 55 °C and the progress of the rection was followed by NMR analysis. After 90 min the starting material had completely disappeared and a new compound was formed in quantitative yield. Removal of the solvent left a crystalline solid, mp 150–151 °C, whose structure was assigned as 2-methyl-2-(1,2,3-triphenyl-2-cyclopropen-1-yl)-4-phenyl-Δ^3-oxazolin-5-one (**11**) on the basis of its spectral properties: IR (KBr) 1768, 1610, 1490, 1443, 1220, 747, 680 cm^{-1}; UV (95% ethanol) 228, 236, 266, 300, 312, 334 nm (ϵ 28 700, 24 400, 17 100, 21 300, 27 600, 19400); NMR ($CDCl_3$, 60 MHz) δ 1.51 (s, 3 H), 6.86–8.33 (m, 15 H); ms, m/e 441, 397, 320, 267.

Anal. Calcd for $C_{31}H_{23}NO_2$: C, 84.33; H, 5.25; N, 3.17. Found: C, 83.93; H, 5.32; N, 3.15.

Preparation of 2-Methyl-4-phenyl-4-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (13). To a solution containing 1.9 mL of diisopropylamine in 32 mL of tetrahydrofuran was added 8.9 mL of a 1.4 M *n*-butyllithium solution at 0 °C. The mixture was allowed to stir at 0 °C for 15 min and then a solution containing 2.17 g of 2-methyl-4-phenyl-Δ^3-oxazolin-5-one in 30 mL of tetrahydrofuran was added to the LDA solution at 0 °C. After stirring at 0 °C for 2 h, the reaction mixture was added to a stirred suspension containing 4.20 g of diphenylmethylcyclopropenyl perchlorate in 80 mL of tetrahydrofuran at −78 °C. After stirring at −78 °C for 4 h, the reaction mixture was allowed to stir for an additional 4 h at room temperature. The solution was quenched with water and the organic layer was concentrated under reduced pressure to give 4.1 g of a crude oil. The oil was chromatographed on a silica gel column using a 3% acetone–hexane mixture as the eluent. The major fraction isolated from the column contained 1.41 g of a yellow solid which was recrystallized from hexane–acetone to give a white solid, p 139–140 °C, whose structure was assigned as 2-methyl-4-phenyl-4-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (**13**) on the basis of its spectral properties: IR (KBr) 3160, 1810, 1790, 1680, 1490, 1440, 1420, 1400, 1340, 1150, 1130, 1132, 1060, 1040, 890, 740, 680 cm^{-1}; UV (95% ethanol) 228, 320, 338 nm (ϵ 18 400, 28 600, 21<<mη400); NMR ($CDCl_3$, 60 MHz) δ 1.40 (s, 3 H), 2.22 (s, 3 H), 6.92–7.83 (m, 15 H); ms, m/e 336, 335, 334, 206, 205.

Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.22; H, 5.59; N, 3.65.

Thermolysis of 2-Methyl-4-phenyl-4-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (13). A solution containing 147 mg of oxazolinone **13** in 1.5 mL of acetonitrile was heated at 138 °C in a sealed tube for 21 min. The solvent was removed under reduced pressure and the residue was chromatographed on a thick-layer plate, using a 3% acetone–hexane mixture as the eluent. The mjaor band contained 80 mg (80%) of a light-yellow oil whose structure was assigned as 2-methyl-2-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)-4-phenyl-Δ^3-oxazolin-5-one (**14**) on the basis of the following spectral data: IR (neat) 1760, 1605, 1485, 1440, 1360, 1190, 1170, 990, 985, 980, 900, 740, 670 cm^{-1}; UV (95% ethanol) 228, 320, 338 nm (ϵ 17 800, 27 600, 21 400); NMR ($CDCl_3$, 60 MHz) δ 1.20 (s, 3 H), 1.34 (s, 3 H), 7.30–8.72 (m, 15 H); ms, m/e 336, 335, 334, 206, 205, 196.

Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.26; H, 5.61; N, 3.40.

To a solution containing 150 mg of **13** in 1.5 mL of acetonitrile was 150 mg of potassium cyanide followed by a catalytic amount of 18-crown-6. The mixture was heated at 100 °C for 2 h. Removal of the solvent left a crude residue, which was chromatographed on a thick layer plate, using a 5% ethyl acetate–hexane solution as the eluent. In addition to oxazolinone 14 (20%), two additional compounds were present. One of these was identified as Δ^3-oxazolinone **9** (30%). The last compound was identified as 1,2-diphenyl-3-methyl-3-cyanocyclopropene (**19**): NMR ($CDCl_3$, 100 MHz) δ 1.67 (s, 3 H, 7.38–7.92 (m, 10 H); IR (neat) 3100, 2353, 1835, 1720, 1600, 1490, 1440, 1300, 1100, 790, 695 cm^{-1}. This material was compared to an independently synthesized sample prepared by treating 3-methyl-1,2-diphenylcyclopropenyl cation with potassium cyanide in the presence of 18-crown-6 in acetonitrile. When the thermolysis of **13** was carried out in acetonitrile that contained 10% of water, a new compound was obtained whose structure was assigned as 3,4-diphenyl-3-buten-2-one (**18**) on the basis of its spectral properties.

Preparation and Thermolysis of 2-Phenyl-4-methyl-4-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (15). A solution containing 2.1 mL of a 1.6 M solution of *n*-butyllithium in hexane was added to a stirred solution containing

(36) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. The infrared absorption spectra were determined on a Perkin-Elmer 467 infrared spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer, using 1-cm matched cells. The proton magnetic resonance spectra were determined at 90 MHz with a Varian Em-390 spectrometer. Mass spectra were determined with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV.

(37) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168.

351 mg of diisopropylamine in 8 mL of tetrahydrofuran at 0 °C under a nitrogen atmosphere. The reaction mixture was allowed to stir at 0 °C for 15 min and then 526 mg of 2-phenyl-4-methyl-Δ^2-oxazolin-5-one (**9**) in 8 mL of tetrahydrofuran was added. After stirring at 0 °C for 2 h, the reaction mixture was transferred to a stirred suspension containing 914 mg of diphenylmethylcyclopropenyl perchlorate in 25 mL of tetrahydrofuran at −78 °C. After stirring for 1 h at −78 °C, the reaction mixture was allowed to stir for an additional 6 h as it warmed to room temperature. After quenching with water, the reaction mixture was concentrated under reduced pressure and the residue was taken up in ether and washed with water. The ether layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to leave behind 1.13 g of a yellow oil. This material was chromatographed on a 1.5 × 100 cm column of silica gel using a 3% acetone–hexane mixture as the eluent. The first compound eluted contained 743 mg (65%) of a solid, mp 106–107 °C, whose structure was assigned as 2-phenyl-4-methyl-4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (**16**) on the basis of its spectral properties: IR ($CHCl_3$) 1815, 1656, 1495, 1445, 1294, 1264, 1156, 1091, 1008, 887, 692 cm^{-1}; UV (cyclohexane) 334, 316, 311, 300, 237, 232 nm (ϵ 22 000, 27 800, 22 000, 20 500, 30 400, 28 000); NMR ($CDCl_3$, 60 MHz) δ 1.17 (s, 3 H), 1.35 (s, 3 H), 7.24–7.66 (m, 6 H), 7.90–8.26 (m, 9 H); ms, *m/e* 335, 320, 205.

Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.34; H, 5.62; N, 3.68.

The second compound eluted from the column contained 164 mg (14%) of a crystalline solid, mp 108–109 °C, whose structure was assigned as 2-phenyl-4-methyl-4-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (**15**): IR ($CHCl_3$) 1795, 1642, 1481, 1437, 1312, 1284, 1151, 1003, 880, 690 cm^{-1}; UV (95% ethanol) 263 nm (ϵ 16 400); NMR ($CDCl_3$, 60 MHz) δ 1.31 (s, 3 H), 2.53 (s, 3 H), 7.05–7.20 (m, 4 H), 7.23–7.57 (m, 7 H), 7.82–8.04 (m, 4 H).

Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.41; H, 5.64; N, 3.63.

A solution containing 150 mg of oxazolinone **15** in 1.5 mL of benzene was heated in a sealed tube at 130 °C for 24 h. Removal of the solvent left a yellow residue, which was purified by silica gel chromatography. The only product present in the reaction was identified as oxazolinone **16**.

Preparation of 2-Methyl-4-allyl-4-phenyl-Δ^2-oxazolin-5-one (21). A solution containing 8.4 mL of 1.6 M *n*-butyllithium in hexane was added to a stirred solution containing 1.04 g of diisopropylamine in 45 mL of tetrahydrofuran at 0 °C under a nitrogen atmosphere. The reaction mixture was allowed to stir at 0 °C for 30 min and then 1.57 g of 2-methyl-4-phenyl-Δ^2-oxazolin-5-one in 45 mL of tetrahydrofuran was added. After stirring at 0 °C for 30 min, the reaction mixture was transferred to a stirred solution containing 3.26 g of allyl bromide in 90 mL of tetrahydrofuran at −78 °C. The reaction mixture was allowed to warm to room temperature over a 4-h period. After quenching with water the mixture was concentrated under reduced pressure, and the resulting residue was taken up in ether and washed with water. The ether solution was dried over magnesium sulfate, and the solvent was removed under reduced pressure to leave behind a dark-brown residue. This material was subjected to silica gel flash chromatography, using a 10% ethyl acetate–hexane mixture as the eluent. The major fraction isolated from the column contained 300 mg (15%) of a yellow oil whose structure was assigned as 2-methyl-4-allyl-4-phenyl-Δ^2-oxazolin-5-one (**21**) on the basis of its spectral properties: NMR ($CDCl_3$, 90 MHz) δ 2.15 (s, 3 H), 2.75 (d, 2 H, J = 7.5 Hz), 5.05–5.97 (m, 3 H), 7.31–7.88 (m, 5 H); IR (neat) 3100, 1822, 1690, 1601, 1490, 1445, 1432, 1380, 1241, 1158, 1055, 900, 746, 690 cm^{-1}; ms, *m/e* 215, 174, 106.

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.60; H, 6.33; N, 6.23.

Thermolysis of 2-Methyl-4-allyl-4-phenyl-Δ^2-oxazolin-5-one (21). A solution containing 300 mg of **21** in 5 mL of a 80:20 mixture of benzene/pyridine was sealed under an argon atmosphere in a Carius tube. The tube was heated at 135 °C in an oil bath for 10 h. After cooling to room temperature, the solvent ws removed under reduced pressure. The resulting residue was chromatographed on a flash silica gel column using a 4% ethyl acetate–hexane mixture as the eluent. The major component isolated from the column contained 92 mg of a yellow oil whose structure was assigned as 2-allyl-2-methyl-4-phenyl-Δ^3-oxazolin-5-one (**22**) on the basis of its spectral properties: IR (neat) 3002, 1779, 1617, 1444, 1262, 1190, 1172, 997, 986, 922, 742, 680 cm^{-1}; NMR (benzene-d_6, 90 MHz) δ 1.39 (s, 3 H), 2.50 (d, 2 H, J = 7.5 Hz), 5.03–5.96 (m, 3 H), 7.36–7.63 (m, 3 H), 8.85–9.03 (m, 2 H); UV (cyclohexane) 264 nm (ϵ 13 250); ms, *m/e* 216, 215, 176, 175, 174, 146.

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.50. Found: C, 72.93; H, 6.27; N, 6.89.

A solution containing 300 mg of **21** in 5 mL of *p*-xylene was heated at 138 °C for 35 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was chromatographed on a flash silica gel column using a 5% ethyl acetate–hexane mixture as the eluent. The major component isolated contained 108 mg (42%) of 2-methyl-6-phenylpyridine (**25**), which was identified by comparison with an authentic sample: NMR ($CDCl_3$, 100 MHz) δ 2.58 (s, 3 H), 6.9–7.6 (m, 6 H), 7.8–8.1 (m, 2 H); IR (neat) 3010, 2900, 1590, 1565, 1475, 1450, 1440, 1360, 1300, 1235, 1157, 1095, 1070, 1025, 803, 758, 735, 694 cm^{-1}. A picrate derivative was formed by adding 5 mL of a saturated picric acid solution in ethanol to 100 mg of the pyridine in 1 mL of ethanol. Recrystallization from 95% ethanol gave yellow crystals, mp 132–133 °C (lit.[38] mp 131–132 °C). The same pyridine was obtained by heating a sample of **22** at 138 °C for 30 h.

A sample of Δ^3-oxazolinone **22** could also be prepared from the photolysis of 2-allyl-2-methyl-3-phenyl-2*H*-azirine (**23**) in the presence of carbon dioxide. A solution containing 100 mg of **23** in 150 mL of benzene was saturated with carbon dioxide. The solution was irradiated for 10 min with a 450-W Hanovia lamp equipped with a Corex filter sleeve. During the irradiation, carbon dioxide was continually bubbled through the solution. The solvent was removed under reduced pressure and the residue was subjected to silica gel flash chromatography, using a 5% ethyl acetate–hexane mixture as the eluent. Removal of the solvent left 84 mg of a yellow oil. Distillation of this material (bp 80 °C (0.015 mm)) gave a pure sample of Δ^3-oxazolinone **22**, which was identical in every detail with a sample obtained from the thermolysis of oxazolinone **21**.

A solution containing 140 mg of **22** in 150 mL of benzene was irradiated for 10 min with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left a yellow oil, which was purified by silica gel chromatography, using a 5% ethyl acetate–hexane mixture as the eluent. The major fraction was identified as Δ^2-oxazolinone **21** by comparison with an authentic sample.

Preparation and Dimerization of 2-Methyl-4-phenyl-Δ^2-oxazolin-5-one (27). A solution containing 3.13 g of *N*-acetyl-*dl*-phenylglycine and 6.23 g of phosphorus pentachloride in 150 mL of carbon tetrachloride was stirred under a nitrogen atmosphere for 4.5 h. The reaction mixture was then cooled to 0 °C and a solution of triethylamine in carbon tetrachloride was slowly added until the solution became basic. The mixture was washed with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 2.92 g (100%) of a dark yellow oil whose structure was tentatively assigned as 2-methyl-4-phenyl-Δ^2-oxazolin-5-one (**27**) on the basis of its spectral properties: NMR (CCl_4, 90 MHz) δ 2.16 (s, 3 H), 5.23 (s, 1 H), 7.40–7.71 (m, 3 H), 8.38–8.58 (m, 2 H); IR (CCl_4) 1800, 1450, 1380, 1200, 1185, 1090, 930, 840 cm^{-1}; ^{13}C NMR ($CDCl_3$) 162.1, 157.2, 133.8, 129.4–129.0 (m), 113.4, 30.1 ppm; ms, *m/e* 174, 146, 104, 103, 78; UV (cyclohexane) 277 nm (ϵ 17 520). Due to the lability of this compound, it was not possible to obtain an analytically pure sample.

A solution containing 130 mg of 2-methyl-4-phenyl-Δ^2-oxazolin-5-one (**27**) in 1.5 mL of carbon tetrachloride was allowed to stand at room temperature for 24 h. The NMR of the solution showed complete conversion of the starting material into two dimeric compounds which could be separated by medium-pressure chromatography, using an 8% ethyl acetate-hexane mixture as the eluent. One of the compounds, mp 119–120 °C, was assigned as the head to head dimer on the basis of its spectral properties: NMR (CCl_4, 90 MHz) 1.64 (s, 3 H), 2.03 (s, 3 H), 7.2–8.4 (m, 10

(38) Bonnier, J. M.; Court, J.; Fay, T. *Bull Chem. Soc. Fr.* **1967**, 1204.

H); IR (CCl_4) 1800, 1450, 1380, 1200, 1185, 1090, 930, 840 cm^{-1}; ms, *m/e* 174, 146, 104, 103, 78; UV (cyclohexane) 273 nm (ϵ 16300); ^{13}C NMR ($CDCl_3$) 162.1, 157.2, 133.8, 129.4–129.0 (m), 113.48, 30.1 ppm.

Anal. Calcd for $C_{20}H_{16}O_4N_2$: C, 68.96; H, 4.63, N, 8.04. Found: C, 68.94; H, 4.64; N, 8.04.

The second dimer, mp 129–130 °C, was too labile to be completely characterized: NMR (CCl_4, 90 MHz) δ 1.70 (s, 3 H), 2.22 (s, 3 H), 7.2–8.5 (m, 10 H); IR (KBr) 3090, 1815, 1785, 1690, 1605, 1450, 1385, 1255, 1210, 1180, 1145, 1070, 995, 925, 775 cm; UV (cyclohexane) 273 nm (ϵ 17004); ms, *m/e* 349 (M^+), 174, 146.

Photolysis of 2-Methyl-4-allyl-4-phenyl-Δ^2-oxazolin-5-one (21). A solution containing 100 mg of **21** in 250 mL of benzene was irradiated for 5 h with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left 80 mg (97%) of an orange oil whose spectral data and chemical behavior were consistent with *N*-(α-allylbenzylidene)acetamide (**33**): NMR (CCl_4, 90 MHz) δ 2.07 (s, 3 H), 3.43–3.50 (m, 2 H), 5.00–5.31 (m, 2 H), 5.66–6.15 (m, 1 H), 7.24–7.55 (m, 3 H), 7.75–7.93 (m, 2 H); IR (neat) 3056, 2916, 2895, 1656, 1596, 1446, 1386, 1261, 1214, 906, 706; UV (cyclohexane) 243 nm (ϵ 3770). Subjection of this material to silica gel flash chromatography, using a 11% ethyl acetate–hexane mixture as the eluent, gave rise to a new compound whose structure was assigned as 1-phenyl-3-buten-1-one on the basis of its spectral characteristics: NMR ($CDCl_3$, 90 MHz) δ 3.56–3.73 (d d, 2 H, *J* = 8.4 Hz, 1 Hz), 5.00–5.30 (m, 2 H), 5.81–6.31 (m, 1 H), 7.23–7.60 (m, 3 H), 7.83–8.13 (m, 2 H); IR (neat) 3085, 2955, 1685, 1600, 1575, 1445, 1330, 1205, 955, 915, 745 cm^{-1}.

The identity of this ketone was verified by comparison with an independently synthesized sample. In a three-neck, 50 mL, round-bottom flask was added 1.0 g of phenyldithiane followed by 10 mL of dry tetrahydrofuran. The flask was cooled to −78 °C and 4 mL of a 1.4 M *n*-butyllithium solution in hexane was slowly added under a nitrogen atmosphere for 20 min. The reaction was kept at −78 °C for 2 h whereupon 740 mg of allyl bromide in 10 mL of tetrahydrofuran was added. After stirring at room temperature for 3 h, the solution was quenched with a saturated ammonium chloride solution. Removal of the solvent under reduced pressure left a yellow oil, which was taken up in ether. The ether layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 1.19 g (98%) of a light-yellow oil. The structure of this compound was assigned as 2-allyl-2-phenyl-1,3-dithiolane on the basis of its spectral data: NMR (CCl_4, 90 MHz) δ 1.67–1.97 (m, 2 H), 2.50–2.80 (m, 6 H), 4.79–5.17 (m, 2 H), 5.34–5.84 (m, 1 H), 7.14–7.50 (m, 3 H), 7.84–7.97 (m, 2 H); IR (neat) 3100, 2975, 2925, 1640, 1598, 1485, 1440, 1425, 1280, 1040, 990, 920, 760 cm^{-1}.

In a 100 mL, three-necked, round-bottom flask were added 1.65 g of *N*-chlorosuccinimide, 3.23 g of silver nitrate, and 40 mL of a 80% acetonitrile–water mixture. To this mixture was added 1 g of 2-allyl-2-phenyl-1,3-dithiolane in 4 mL of acetonitrile. The reaction was left stirring at room temperature for 1 h after which 4 mL of a saturated aqueous sodium sulfite solution, 4 mL of a saturated sodium carbonate solution, and finally 4 mL of a saturated sodium chloride solution were added. The organic layer was filtered through Celite and concentrated under reduced pressure. The residue was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left 1-phenyl-3-buten-1-one as a pale oil, which was identical in every detail with a sample obtained from the hydrolysis of acetimide **33**.

Preparation of 2-Methyl-4-(3-methyl-2-butenyl)-4-phenyl-Δ^2-oxazolin-5-one (29). A solution containing 430 mg of 2-methyl-4-phenyl-Δ^3-oxazolin-5-one (**9**), 1.04 g of 3-methyl-2-butenyl bromide, 100 mg of potassium iodide, and 516 mg of *N,N*-diisopropylethylamine in 30 mL of dimethylformamide was heated at 90 °C for 5 h. After the reaction mixture had cooled to room temperature, 100 mL of an aqueous ammonium chloride solution was added and the solution was extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a crude yellow oil. The oil was purified by flash chromatography, using an 8% ethyl acetate–hexane solution as the eluent, to give 373 mg (80%) of a nearly colorless oil. Distillation of this material (bp 80 °C (0.4 mm)) gave a colorless oil that was assigned as 2-methyl-4-(3-methyl-2-butenyl)-4-phenyl-Δ^2-oxazolin-5-one (**29**) on the basis of the following data: IR (neat) 3075, 3045, 2990, 2930, 1825, 1694, 1602, 1500, 1446, 1431, 1376, 1238, 1059, 897, 688 cm^{-1}; NMR (CCl_4, 90 MHz) δ 1.55 (s, 3 H), 1.67 (s, 3 H), 2.40 (s, 3 H), 2.66 (d, 2 H, *J* = 8.0 Hz), 4.98 (t, 1 H, *J* = 8 Hz), 7.2–8.8 (m, 5 H); ms, *m/e* 243 (M^+), 215, 199, 174; UV (cyclohexane) 256 nm (ϵ 1400).

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.06; H, 7.09; N, 5.74.

Thermolysis of 2-Methyl-4-(3-methyl-2-butenyl)-4-phenyl-Δ^2-oxazolin-5-one (29). A solution containing 250 mg of **29** in 5 mL of a 80:20 benzene/pyridine mixture was sealed under an argon atmosphere in a Carius tube. The tube was heated at 162 °C for 40 h. After cooling to room temperature, the solvent was removed and the residue was chromatographed, using a 5% ethyl acetate–hexane mixture as the eluent. The major fraction was a clear oil whose structure was assigned as 2-(1,1-dimethyl-2-propenyl)-2-methyl-4-phenyl-Δ^2-oxazolin-5-one (**30**) on the basis of its spectral data: IR (neat) 3079, 3048, 2988, 2924, 1775, 1640, 1602, 1500, 1460, 1400, 1275, 948, 745 cm^{-1}; NMR (benzene-d_6, 90 MHz) δ 1.26 (s, 6 H), 1.60 (s, 3 H), 4.77–4.80 (m, 2 H), 6.02 (dd, 1 H, *J* = 18.0, 11.0 Hz), 6.94–7.79 (m, 5 H); UV (cyclohexane) 260 nm (ϵ 10000); ms, *m/e* 243 (M^+), 215, 199, 174.

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.01; H, 7.08; N, 5.74.

Preparation and Irradiation of 2-Methyl-2-(3-methyl-2-butenyl)-4-phenyl-Δ^3-oxazolin-5-one (31). A solution containing 100 mg of 2-methyl-2-(3-methyl-2-butenyl)-3-phenyl-2*H*-azirine (**32**) in 1540 mL of benzene was saturated with carbon dioxide. The solution was irradiated for 15 min with a 450-W Hanovia lamp equipped with a Corex filter sleeve. During the irradiation, carbon dioxide was continually bubbled through the solution. Removal of the solvent under reduced pressure left a yellow residue, which was subjected to silica flash chromartography, using a 5% ethyl acetate–hexane mixture as the eluent. The first component isolated from the column contained 79 mg (41%) of a pale-yellow oil. Distillation of the residue (bp 65° C (0.01 mm)) gave a colorless oil whose structure was assigned as 2-methyl-2-(3-methyl-2-butenyl)-4-phenyl-Δ^3-oxazolin-5-one (**31**) on the basis of the following data: IR (neat) 2998, 2940, 1773, 1640, 1578, 1490, 1450, 1355, 1270, 1240, 1181, 1008, 997, 902, 812, 693 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.56 (s, 3 H), 1.96 (br s, 6 H), 2.61 (d, *J* = 7.5 Hz, 5 H), 5.00 (t, 1 H), 7.43–7.59 (m, 3 H), 8.26–8.43 (m, 2 H); ms, *m/e* 243, 199, 184, 175, 131, 130; UV (cyclohexane) 264 nm (ϵ 12300).

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.28; H, 6.83; N, 6.14.

A solution containing 120 mg of Δ^3-oxazolinone **31** in 200 mL of benzene was irradiated for 30 min with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left a clear oil whose structure was identical with that of a sample prepared from the alkylation of 2-phenyl-4-methyl-Δ^3-oxazolinone with prenyl bromide.

Photodecarbonylation of 2-Methyl-4-(3-methyl-2-butenyl)-4-phenyl-Δ^2-oxazolin-5-one (29). A solution containing 100 mg of **29** in 130 mL of benzene was irradiated under an argon atmosphere for 3 h with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure gave 82 mg of a yellow oil whose spectral data was consistent with *N*-(α-prenylbenzylidene) acetamide (**34**): IR (neat) 3075, 3045, 2990, 2930, 1645, 1602, 1500, 1446, 1431, 1376, 1238, 897 cm^{-1}; NMR (CCl_4, 90 MHz) δ 1.66 (s, 6 H), 2.09 (s, 3 H), 3.36 (s, 2 H, *J* = 7 Hz), 5.14 (t, 1 H, *J* = 7 Hz), 7.1–8.9 (m, 5 H); ms, *m/e* 215 (M^+), 146, 103; UV (cyclohexane) 244 nm (ϵ 4937).

Flash chromatography of **34** with an 8% ethyl acetate–hexane mixture gave 50 mg of a clear oil whose physical properties were identical in every detail with that of an authentic sample of 4-methyl-1-phenyl-3-penten-1-one (bp 118 °C (0.06 mm)) prepared by the method of Cantrell;[39] NMR (CCl_4, 90 MHz) δ 1.67 (s, 3 H), 1.73 (s, 3 H), 3.55 (d, 2 H, *J* = 7 Hz), 5.40 (t, 1 H, *J* = 7 Hz), 7.30–8.00 (m, 5 H); IR (neat) 3065, 2975, 2930, 1687, 1600, 1562, 1450, 1378, 1320, 1280, 1210, 1185, 985, 750, 690 cm^{-1}; UV (cyclohexane) 238 nm (ϵ 5420).

(39) Cantrell, T. S. *J. Org. Chem.* **1977**, *42*, 4238.

Photolysis of 2,4-Dimethyl-4-phenyl-Δ^2-oxazolin-5-one (36). A solution containing 200 mg of 2,4-dimethyl-4-phenyl-Δ^2-oxazolin-5-one (**36**) in 250 mL of benzene was irradiated for 5 h with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left 187 mg (100%) of an orange oil whose spectral data and chemical behavior were consistent with *N*-(α-methylbenzylidene)acetamide (**37**): NMR (CCl_4, 90 MHz) δ 1.99 (s, 3 H), 2.17 (s, 3 H), 7.08–7.43 (m, 3 H), 7.66–7.86 (m, 2 H); IR (neat) 3065, 2925, 1690, 1640, 1585, 1450, 1375, 1365, 1300, 1225, 1035, 770, 700, 620 cm^{-1}. Subjection of this material to silica gel flash chromatography, using an 11% ethyl acetate-hexane mixture as the eluent, resulted in hydrolysis to acetophenone and acetamide.

A 170-mg sample of *N*-(α-methylbenzylidene)acetamide (**37**) in 6 mL of benzene was treated with 2.2 mL of triethylamine for 36 h. Removal of the solvent left a yellow residue, which was chromatographed on a flash silica gel column using a 30% ethyl acetate–hexane mixture as the eluent. The major fraction isolated contained 87 mg (51%) of a crystalline solid, mp 90–91 °C, whose structure was assigned as *N*-(1-phenylvinyl)acetamide (**35**) on the basis of the following data: NMR (CCl_4, 90 MHz) δ 2.03 (s, 3 H), 5.11 (br s, 1 H), 5.79 (br s, 1 H), 6.95–7.25 (br s, 1 H), 7.27–7.55 (m, 5 H); IR (neat) 3260, 3030, 1670, 1640, 1535, 1400, 1390, 1370, 1355, 1340, 1050, 810, 795, 705, 650, 545 cm^{-1}; UV (cyclohexane) 248 nm (ϵ 6300); ms, *m/e* 161, 120, 119, 105.

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.52; H, 6.89; N, 8.68.

The identity of this material was verified by comparison with an independently synthesized sample. To a solution containing 2.58 g of benzonitrile in 5.0 mL of ether was added 9.47 mL of a 2.64 M solution of methylmagnesium bromide in 30 mL of ether. The mixture was heated at reflux for 15 min and cooled to room temperature and was then quenched by the addition of 1.96 g of acetyl chloride in 5.0 mL of ether. The resulting mixture was heated at reflux for 15 min and was then decomposed with 5.0 mL of a saturated ammonium chloride solution. The ether layer was separated, washed with 10 mL of water, and dried over sodium sulfate. Removal of the solvent under reduced pressure left 2.71 g of an orange oil. This oil consisted of acetophenone, benzonitrile, and *N*-(1-phenylvinyl)acetamide (**35**).

Preparation of 2-Methyl-4-ethyl-4-phenyl-Δ^2-oxazolin-5-one. A solution containing 430 mg of **9**, 763 mg of ethyl bromide, 100 mg of potassium iodide, and 516 mg of *N,N*-diisopropylethylamine in 30 mL of dimethylformamide was heated at 90 °C for 5 h. After the reaction mixture had cooled to room temperature, 100 mL of an aqueous ammonium chloride solution was added and the solution was extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a crude yellow oil. The residue was purified by flash chromatography, using an 8% ethyl acetate–hexane mixture as the eluent, to give 302 mg (74%) of a clear oil. Distillation of the residue (bp 75 °C (0.01 mm)) gave a colorless oil whose structure was assigned as 2-methyl-4-ethyl-4-phenyl-Δ^2-oxazolin-5-one on the basis of the following spectral data: IR (neat) 3070, 2980, 2944, 1820, 1690, 1604, 1495, 1450, 1438, 1375, 1250, 1170, 1062, 910, 750, 700, 655 cm^{-1}; NMR (CCl_4, 90 MHz) δ 0.83 (t, 3 H, J = 8 Hz), 1.98 (q, 2 H, J = 8 Hz), 2.22 (s, 3 H), 7.2–7.8 (m, 5 H); ms, *m/e* 203 (M^+), 175, 159; UV (cyclohexane) 257 nm (ϵ 2000).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.67; H, 6.49; N, 6.83.

Photodecarbonylation of 2-Methyl-4-ethyl-4-phenyl-Δ^2-oxazolin-5-one. A solution containing 300 mg of the above compound in 130 mL of benzene was irradiated under an argon atmosphere for 3 h with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left 250 mg of a yellow oil that was identified as *N*-(α-ethylbenzylidene)acetamide on the basis of its physical data: NMR (CCl_4, 90 MHz) δ 1.17 (t, 3 H, J = 7 Hz), 2.07 (s, 3 H), 2.65 (q, 2 H, J = 7 Hz), 7.1–8.0 (m, 5 H); ms, *m/e* 175 (M^+), 146, 103; UV (cyclohexane) 243 nm (ϵ 7100); IR (neat) 3070, 2980, 2944, 1647, 1604, 1494, 1450, 1220, 1060, 905, 775, 695 cm^{-1}. Flash chromatography of this material with an 8% ethyl acetate–hexane mixture gave 110 mg of a clear liquid whose physical properties were idential in every detail with those of an authentic sample of propiophenone: NMR (CCl_4, 90 MHz) δ 1.14 (t, 3 H, J = 7 Hz), 2.85 (q, 2 H, J = 7 Hz), 7.20–8.00 (m, 5 H); IR (neat) 3065, 2985, 2945, 2885, 1685, 1600, 1587, 1452, 1358, 1225, 1186, 1080, 1018, 955, 746, 690 cm^{-1}.

Preparation of 2-Methyl-4-benzyl-4-phenyl-Δ^2-oxazolin-5-one. A solution containing 430 mg of 4-methyl-2-phenyl-Δ^3-oxazolin-5-one (**9**), 1.20 g of benzyl bromide, 100 mg of potassium iodide, and 516 mg of *N,N*-diisopropylethylamine in 30 mL of dimethylformamide was heated at 90 °C for 5 h. After the reaction mixture had cooled down to room temperature, 100 mL of an aqueous ammonium chloride solution was added and the solution was extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a crude yellow oil. The oil was purified by flash chromatography, using an 8% ethyl acetate–hexane mixture as the eluent. Distillation of the residue (bp 86 °C (0.09 mm)) gave 387 mg (73%) of a colorless oil whose structure was assigned as 2-methyl-4-benzyl-4-phenyl-Δ^2-oxazolin-5-one on the basis of the following data: IR (neat) 3098, 3075, 3044, 2970, 2940, 1820, 1690, 1604, 1500, 1455, 1437, 1388, 1250, 1065, 964, 912, 795, 760, 727 cm^{-1}; NMR (CCl_4, 90 MHz) δ 1.82 (s, 3 H), 3.20 (s, 2 H), 7.0–7.8 (m, 10 H); ms, *m/e* 265 (M^+), 237, 221, 146; UV (cyclohexane) 256 nm (ϵ 1600).

Photodecarbonylation of 4-Benzyl-2-methyl-4-phenyl-Δ^2-oxazolin-5-one. A solution containing 180 mg of the above compound in 130 mL of benzene was irradiated under an argon atmosphere for 3 h with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Evaporation of the solvent under reduced pressure left 158 mg of a yellow oil whose spectral data were consistent with *N*-(α-benzylbenzylidene)acetamide: NMR (CCl_4, 90 MHz) δ 1.82 (s, 3 H), 3.77 (s, 2 H), 7.0–8.0 (m, 10 H); IR (neat) 3098, 3075, 3044, 2970, 2940, 1644, 1572, 1500, 1455, 1437, 1388, 1364, 1250, 1220, 1065, 964, 910, 795, 760, 727 cm^{-1}; ms *m/e* 237 (M^+), 146, 103; UV (cyclohexane) 248 nm (ϵ 3300). Flash chromatography of this material with an 8% ethyl acetate–hexane mixture gave 36 mg of a white crystalline solid, mp 59–60 °C, whose physical properties were identical in every detail with those of an authentic sample of deoxybenzoin: NMR (CCl_4, 90 MHz) δ 4.19 (s, 2 H), 7.20–8.00 (m, 10 H); IR (eat) 3058, 3030, 1672, 1587, 1575, 1493, 1445, 1333, 1267, 1215, 1176 cm^{-1}.

Preparation and Thermolysis of 2-Phenyl-4-allyl-4-methyl-Δ^2-oxazolin-5-one (38). A solution containing 1.04 g of 2-phenyl-4-methyl-Δ^2-oxazolin-5-one (**41**), 1.44 g of allyl bromide, 1.53 g of *N,N*-diisopropylethylamine, and 300 mg of potassium iodide in 30 mL of dimethylformamide was heated at 90 °C under a nitrogen atmosphere for 5 h. After allowing the reaction mixture to cool to room temperature, the solution was quenched with a saturated ammonium chloride solution. Removal of the solvent under reduced pressure left a crude yellow residue, which was taken up in ether. The ether layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give 1.10 g of a yellow oil. This material was purified by flash chromatography on a silica gel column using a 9% ethyl acetate–hexane mixture as the eluent to give 890 mg (70%) of 2-phenyl-4-allyl-4-methyl-Δ^2-oxazolin-5-one (**38**) as a clear oil whose structure was assigned on the basis of the following data: NMR ($CDCl_3$, 90 MHz) δ 1.41 (s, 3 H), 2.45 (d, 2 H, J = 8.2 Hz), 4.92–5.86 (m, 3 H), 7.21–7.57 (m, 3 H), 7.85–8.04 (m, 2 H); IR (neat) 3000, 1825, 1670, 1440, 1315, 1285, 1165, 1055, 995, 895, 875, 760, 685 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.62; H, 6.14; N, 6.48.

A 125-mg sample of **38** in 1.5 mL of a 80:20 benzene/pyridine mixture was heated in a sealed tube at 175 °C for 143 h. Removal of the solvent followed by thick-layer chromatography gave 2-methyl-6-phenylpyridine (**25**) as the major product.

A solution containing 170 mg of **38** in 250 mL of benzene was irradiated for 13 h with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure gave 103 mg (73%) of 2-phenyl-4-methyl-Δ^2-oxazolin-5-one (**41**) as a clear oil. The structure of this material was verified by comparison with an independently synthesized sample: NMR ($CDCl_3$, 60 MHz) δ 1.47 (d, 3 H, J = 7.0 Hz), 4.31 (q, 3 H, J = 7.0 Hz), 7.26–8.03 (m, 5 H).

Preparation of 2-Phenyl-4-methyl-4-(3-methyl-2-butenyl)-Δ^2-oxazolin-5-one (39). A solution containing 430 mg of 2-phenyl-4-methyl-Δ^2-oxazolin-5-one (**41**), 1.04 g of 3-methyl-2-

butenyl bromide, 100 mg of potassium iodide, and 516 mg of *N,N*-diisopropylethylamine in 30 mL of dimethylformamide was heated at 90 °C for 5 h. After the reaction mixture had cooled to room temperature, 100 mL of an aqueous ammonium chloride solution was added and the mixture was extracted with ether. The ethereal layer was washed with water, dried over magnesium sulfate, and concentrated under reduced pressure to give a crude yellow oil. The oil was purified by flash chromatography, using an 8% ethyl acetate–hexane mixture as the eluent. The major fraction contained 398 mg (82%) of a nearly colorless oil. Distillation of this material (bp 80 °C (0.04 mm)) gave a colorless oil, which was assigned as 2-phenyl-4-methyl-4-(3-methyl-2-butenyl)-Δ^2-oxazolin-5-one (**39**) on the basis of the following data: NMR (CCl_4, 90 MHz) δ 1.47 (s, 3 H), 1.63 (s, 6 H), 2.49 (d, 2 H, J = 8 Hz), 5.02 (t, 1 H, J = 8 Hz), 7.3–8.0 (m, 5 H); IR (neat) 3085, 3065, 3000, 2960, 2940, 1805, 1650, 1620, 1580, 1505, 1464, 1400, 1340, 1315, 1040, 935, 910, 825, 740 cm^{-1}; ms *m/e* 243 (M^+), 215, 199, 174; UV (cyclohexane) 243 nm (ϵ 16 800).

Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.01; H, 7.08; N, 5.74.

Thermal and Photochemical Behavior of 2-Phenyl-4-methyl-4-(3-methyl-2-butenyl)-Δ^2-oxazolin-5-one (39). A solution containing 181 mg of **39** in 130 mL of benzene was irradiated under an argon atmosphere for 5 h with a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left 140 mg of 2-phenyl-4-methyl-Δ^2-oxazolin-5-one (**41**). The structure of this material was verified by comparison with an authentic sample. Heating a sample of **39** in a 80:20 benzene/pyridine mixture at 155 °C for 16 h gave 2-phenyl-2-(1,1-dimethyl-2-propenyl)-4-methyl-Δ^3-oxazolin-5-one (**40**): NMR ($CDCl_3$, 90 MHz) δ 3.73 (dd, 1 H, J = 16.0, 10.0 Hz), 3.03 (dd, 1 H, J = 16.0, 10.0 Hz).

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Registry No. **9**, 52755-67-6; **10**, 84537-26-8; **11**, 79998-98-4; **12**, 41728-97-6; **13**, 79999-05-6; **14**, 79999-06-7; **15**, 84537-27-9; **16**, 79998-99-5; **18**, 1722-69-6; **19**, 84537-28-0; **21**, 79402-65-6; **22**, 79402-66-7; **23**, 56434-95-8; **25**, 46181-30-0; **25** picrate, 56434-99-2; **26**, 29633-99-6; **27**, 46173-12-0; **27** dimer, 84537-36-0; **28**, 84537-29-1; **29**, 79402-67-8; **30**, 79402-68-9; **31**, 79402-69-0; **32**, 62737-00-2; **33**, 84537-30-4; **34**, 79402-70-3; **35**, 57957-24-1; **36**, 4855-22-5; **37**, 52762-80-8; (±)-**38**, 84620-27-9; (±)-**39**, 84537-31-5; (±)-**40**, 84537-32-6; (±)-**41**, 51127-13-0; 3-methyl-2-phenylazirine, 16205-14-4; *N*-benzoyl-DL-alanine, 1205-02-3; triphenylcyclopropenyl perchlorate, 58003-32-0; diphenylmethylcyclopropenyl perchlorate, 84537-34-8; allyl bromide, 106-95-6; 1-phenyl-3-buten-1-one, 6249-80-5; 2-allyl-2-phenyl-*m*-dithiane, 84537-35-9; 3-methyl-2-butenyl bromide, 870-63-3; 4-methyl-1-phenyl-3-penten-1-one, 36597-09-8; benzonitrile, 100-47-0; methyl bromide, 74-83-9; 2-methyl-4-ethyl-4-phenyl-Δ^2-oxazolin-5-one, 4855-25-8; *N*-(α-ethylbenzylidene)acetamide, 79402-71-4; 2-methyl-4-benzyl-4-phenyl-Δ^2-oxazolin-5-one, 79402-73-6; *N*-(α-benzylbenzylidene)acetamide, 79402-72-5.

Reaction of Phosphorus Pentachloride with 2-Acetylthiophene and Acetophenone

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The treatment of 2-acetylthiophene with PCl_5, followed by dehydrochlorination, is known to be a poor method for synthesizing 2-ethynylthiophene (**1a**). Reinvestigation of the reaction showed the major products to be the *E* and *Z* isomers of 1,2-dichloro-1-(2-thienyl)ethylene (**7a**), with minor amounts of 1,1-dichloro-1-(2-thienyl)ethane (**3a**), 1-chloro-1-(2-thienyl)ethylene (**4a**), 2-(chloroacetyl)thiophene, and 2-(dichloroacetyl)thiophene. The treatment of acetophenone with PCl_5 yielded similar products, and the mechanism of these reactions is discussed. The major product **7a** could be converted into **1a** by reaction with magnesium. The yield of **4a** was increased when pyridine was also used, when only 1 equiv of PCl_5 was added by portions to the ketone, or when catecholphosphorus trichloride was used instead of PCl_5. The best method for converting 2-acetylthiophene into **1a** goes through the enol phosphonate of 2-(bromoacetyl)thiophene, which is treated with sodium amide.

The treatment of carbonyl compounds with phosphorus pentachloride, followed by double dehydrochlorination of the resulting *gem*-dichloro derivatives, constitutes a classical synthesis of acetylenic compounds.[1,2] Nord and his

$$RCOCH_3 + PCl_5 \rightarrow RCCl_2CH_3 \rightarrow \underset{\mathbf{1}}{RC{\equiv}CH}$$

co-workers applied it to the synthesis of 2-ethynylthiophene (**1a**) from 2-acetylthiophene (**2a**)[3,4] and assumed to have obtained a mixture of 1,1-dichloro-1-(2-thienyl)-ethane (**3a**) and 1-chloro-1-(2-thienyl)ethylene (**4a**), but no pure products were isolated. Their increase in yield from 20–22%[3] to 65%[4] was attributed to the dehydrochlorination procedure. Difficulties with this synthesis were noted,[5] but a full analysis remained to be performed. In this report, the details of the reaction of PCl_5 with **2a** and with the related acetophenone are described, as well as improved methods for obtaining **1a**.

Results and Discussion

The main products of the reaction of **2a** with PCl_5 were analyzed by NMR and by GLC–mass spectroscopy and identified as **3a**, **4a**, **6a**, and **7a** (Scheme I). The major product was **7a** (a mixture of *E* and *Z* isomers accounting for 51% of the isolated products) rather than the expected **3a** and **4a**. Its formation illustrates one danger associated

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