36912-30-8; *trans*-**1** (2-OC_6H_5 derivative), 36895-18-8; *cis*-**2**, 74737-11-4; *trans*-**2**, 74737-10-3; *trans*-**3**, 50600-54-9; *cis*-**3** (2-OC_6H_4-*p*-Me derivative), 50378-57-9; *trans*-**3** (2-OC_6H_4-*p*-Me derivative), 50378-50-2; *cis*-**3** (2-OC_6H_5 derivative), 50378-58-0; *trans*-**3** (2-OC_6H_5 derivative), 50378-51-3; *cis*-**3** (2-OMe derivative), 88157-75-9; *trans*-**3** (2-OMe derivative), 88157-76-0; *cis*-**3** (2-OEt derivative), 88157-77-1; *trans*-**3** (2-OEt derivative), 88157-78-2; *cis*-**3** (2-OPr-*i* derivative), 88157-79-3; *trans*-**3** (2-OPr-*i* derivative), 88157-80-6; *cis*-**3** (2-OCH_2CCl_3 derivative), 88157-81-7; *trans*-**3** (2-OCH_2CCl_3 derivative), 88157-82-8; *cis*-**3** (2-$OCH_2CH{=}CH_2$ derivative), 88157-83-9; *trans*-**3** (2-$OCH_2CH{=}CH_2$ derivative), 88157-84-0; *cis*-**4**, 74737-12-5; *trans*-**4**, 74737-13-6; **5**-*ax*, 74410-72-3; **5**-*ax* (2-OEt derivative), 88199-18-2; **5**-*eq* (2-OEt derivative), 88199-19-3; **5**-*ax* (2-OCH_2CCl_3 derivative), 78339-64-7; **5**-*eq* (2-OCH_2CCl_3 derivative), 78266-97-4; **5**-*ax* (2-OC_6H_5 derivative), 74378-77-1; **5**-*eq* (2-OC_6H_5 derivative), 74410-66-5; **5**-*ax* (2-OC_6H_4-*p*-Me derivative), 78339-63-6; **5**-*eq* (2-OC_6H_4-*p*-Me derivative), 78266-96-3; 6-*ax*, 78339-65-8; 6-*eq*, 78266-98-5; *trans*-**7**, 78266-87-2; *cis*-**8**, 78266-89-4; *trans*-**8**, 36912-28-4; CsF, 13400-13-0; F^-, 16984-48-8; phosphorus oxychloride, 10025-87-3; *trans*-2-(hydroxymethyl)-1-cyclohexanol, 7429-40-5.

On the Mechanism of the Thermal Conversion of Cyclopropenyl-Substituted Oxazolinones to Pyridines

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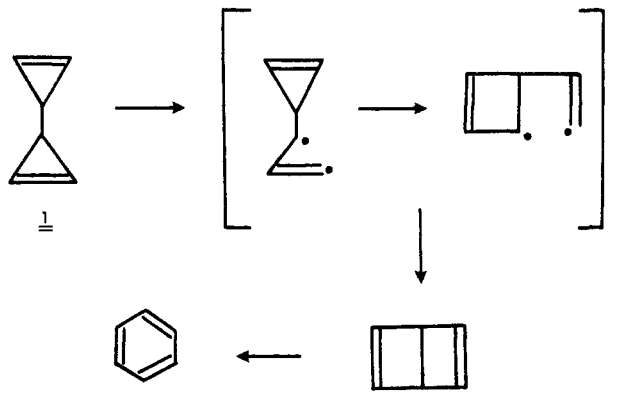
Abstract: Thermolysis or photolysis of a sample of a 3-cyclopropenyl-substituted 2*H*-azirine produced 2-methyl-3,4,5,6-tetraphenylpyridine in high yield. The reaction can best be rationalized by a mechanism involving formation of a nitrile ylide intermediate followed by intramolecular dipolar cycloaddition to give an azabenzvalene, which subsequently rearranges to the pyridine. The thermal chemistry of a series of cyclopropenyl-substituted oxazolinones was also investigated. These oxazolinones undergo a thermally induced 1,3-dipolar cycloreversion reaction with elimination of carbon dioxide to generate a nitrile ylide intermediate adjacent to the cyclopropene ring. This dipole can be trapped when the thermolysis of the oxazolinone was carried out in the presence of a reactive dipolarophile. Heating a sample of 2-phenyl-4-methyl-4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one at 150 °C for 24 h afforded a mixture of 2,3-dimethyltriphenylpyridine (45%), 2,4-dimethyltriphenylpyridine (20%), and 2,5-dimethyltriphenylpyridine (35%). The formation of these products is proposed to involve a stepwise cycloaddition of the initially generated nitrile ylide to produce a bicyclobutyl zwitterion which can either collapse to give an azabenzvalene or undergo rearrangement to a cyclobutenyl cation. This latter species closes to produce two different aza Dewar benzenes. Reorganization of the azabenzvalene and aza Dewar benzenes gives rise to the observed pyridines. Alternate mechanisms based on a concerted intramolecular cycloaddition reaction of the nitrile ylide do not account for the observed product ratios.

Small-ring compounds are particularly interesting species because their high energy content relative to the acyclic isomers often endows them with unusual reactivity patterns.[1-4] Studies dealing with the chemical reactions of unsaturated three-ring systems have played an important role in the development of our understanding of the mechanism by which carbon–carbon bonds may be broken and reformed.[5] During the last few years the chemistry of 3,3′-bicyclopropenyls has attracted considerable interest.[6-13] The rearrangement of these compounds to benzene derivatives is one of the most exothermic unimolecular isomerizations known (Scheme I). Its mechanism has been a source of controversy over the years. At various times the rearrangement has been postulated to proceed through Dewar benzene,[8] benzvalene,[14] prismane,[6] and diradical[11] and ionic intermediates.[8] The most recent data are consistent with a path involving initial homolytic cleavage of one of the cyclopropene rings followed by expansion of the other ring, closure to a Dewar benzene, and finally opening of the Dewar intermediate to form aromatic products.[12,13] The conversion of the closely related 3-azirinylcyclopropene system (**2**) to a pyridine derivative **5** represents a more complicated transformation since several different possibilities are available (Scheme II). One of the more attractive paths involves the initial formation of a nitrile ylide intermediate[15] **3**, followed by intramolecular dipolar cycloaddition[16] to give azabenzvalene **5** which subsequently rearranges to pyridine **4**.[17] This paper describes some of our observations in this area with particular reference to the mechanism of the rearrangement.

Scheme I



Results

Earlier work in the literature has shown that the synthesis of 2*H*-azirines based on the modified Neber reaction proceeds in high yield if the α-hydrogen is tertiary or benzylic.[18] This is probably related to the fact that the mechanism of the Neber rearrangement

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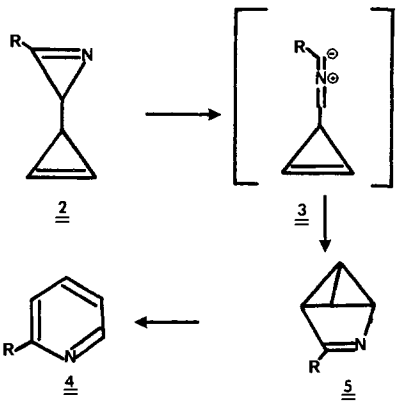
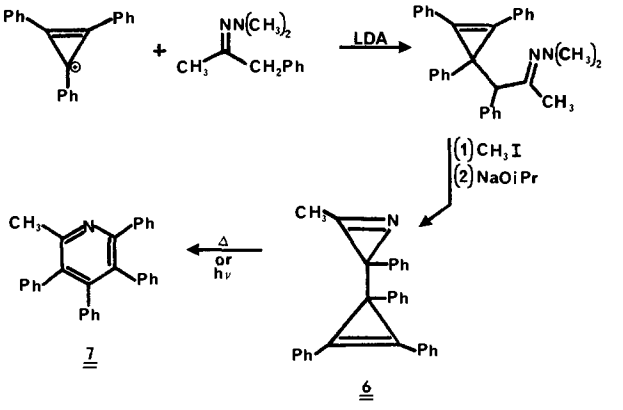
Scheme II



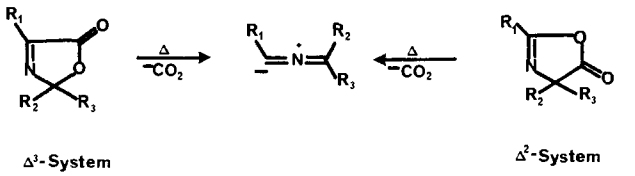
involves the formation of a species resembling a vinyl nitrene which undergoes subsequent cyclization.[19] With this in mind, we prepared azirinylcyclopropene **6** in good yield by treating tri-



phenylcyclopropenyl perchlorate with the anion derived from phenylacetone *N,N*-dimethylhydrazone, followed by quaternarization with methyl iodide and treatment of the salt with sodium isopropoxide. Thermolysis or photolysis of a sample of the cyclopropenyl-substituted 2*H*-azirine **6** produced 2-methyl-3,4,5,6-tetraphenylpyridine (**7**), mp 160–161 °C, in quantitative yield.[20] We believe that the rearrangement of **6** to **7** occurs via the sequence of reactions described in Scheme II.

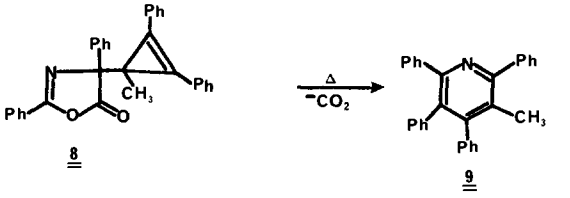
In order to provide additional support for this mechanism, we decided to synthesize a series of related azirinyl-substituted cyclopropenes via the Neber approach. Although it was possible to prepare the appropriate trimethylhydrazonium salts as outlined above, all attempts to convert them into the desired azirinylcyclopropene system were unsucessful and consequently this approach was abandoned.

In view of our lack of success in preparing an appropriately labeled azirinylcyclopropene, an alternate approach was used to generate a nitrile ylide adjacent to a cyclopropene ring. Earlier results in the literature have shown that trisubstituted oxazolinones readily lose carbon dioxide at moderate temperatures to form products expected from nitrile ylides.[21-26] If the dipole contains



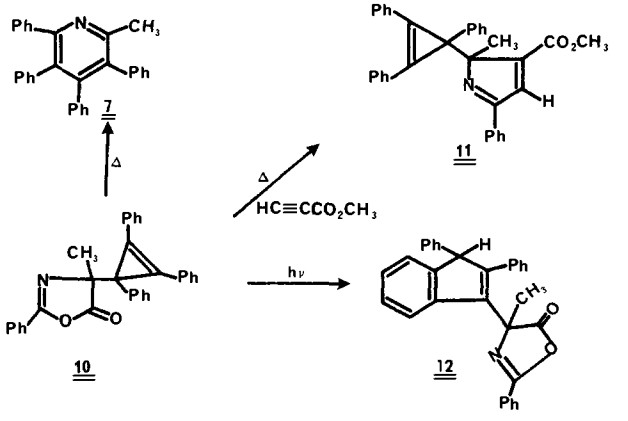
groups capable of conjugation, 1,5-electrocyclization is observed.[23] When alkyl groups are present on the nitrile ylide carbon centers, the dipole can be trapped with various dipolarophiles.[24-29]

We reasoned that a cyclopropenyl-substituted oxazolinone would be an appropriate precursor for the generation of the desired dipolar intermediate (i.e., **3**). The first system we studied involved thermolysis of Δ^2-oxazolinone **8**. The synthesis of **8** was ac-



complished by treating the anion derived from 2,4-diphenyl-Δ^2-oxazolinone with diphenylmethylcyclopropenyl perchlorate. The initial alkylation step proceeded quite smoothly and analogously to that reported by Steglich and Lohmar.[30] This group had previously shown that treatment of Δ^2-oxazolinones with base in the presence of an alkyl halide always gives the 4-substituted Δ^2-oxazolinone ring system. Heating oxazolinone **8** at 111 °C in toluene resulted in the quantitative formation of a single product, mp 185–186 °C, whose structure was assigned as 3-methyl-2,4,5,6-tetraphenylpyridine (**9**) on the basis of its spectral properties and by comparison with an independently synthesized sample.[31]

Attention was next turned to the thermal behavior of the closely related Δ^2-oxazolinone **10**. Heating a sample of **10** at 130 °C



in xylene for 24 h resulted in a quantitative yield of pyridine **7**. When the thermolysis of **10** was carried out in xylene in the

(11) Weiss, R.; Kobl, H. *J. Am. Chem. Soc.* **1975**, *97*, 3222, 3224.
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(16) For leading references of intramolecular cycloadditions of nitrile ylides, see: Padwa, A.; Ku, A.; Carlsen, P. H. J. *J. Am. Chem. Soc.* **1978**, *100*, 3494.
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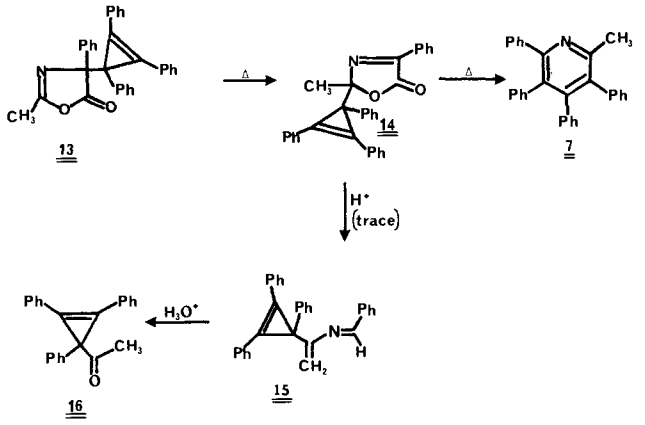
(31) Moerck, R. E.; Battiste, M. A. *Tetrahedron Lett.* **1972**, 303.

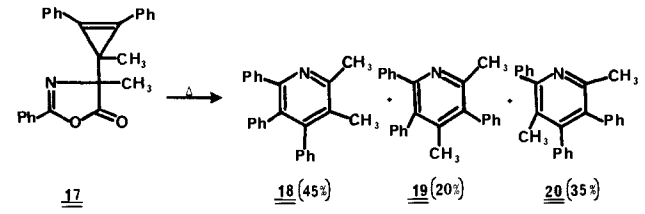
presence of methyl propiolate, 2*H*-pyrrole **11**, mp 159–160 °C, was isolated in good yield. Under these conditions, the formation of **7**, which is produced in quantitative yield in the absence of a trapping reagent, is entirely suppressed. In marked contrast to the thermal results, the photolysis of **10** did not result in the extrusion of carbon dioxide but rather produced the indenyl-substituted Δ^2-oxazolinone **12**.

The thermal behavior of the isomeric Δ^2-oxazolinone **13** was also studied. Heating a sample of **13** at 55 °C for 90 min produced the Δ^3-isomer **14** in quantitative yield. Further heating of **14**

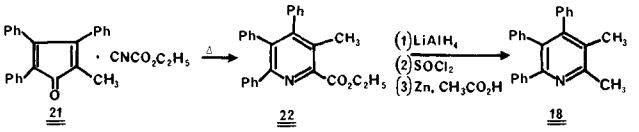


at 180 °C for 35 h afforded pyridine **7** as the exclusive product. The formation of **7** can be postulated to arise by extrusion of carbon dioxide from **14** to give a nitrile ylide intermediate which undergoes subsequent reorganization to pyridine **7** according to the mechanism outlined in Scheme II. When the thermolysis of **14** was carried out in the presence of a trace of acid, azadiene **15** was also formed (78%). This material was readily converted to 3-acetyltriphenylcyclopropene **16** on treatment with water. The formation of **15** from **14** is an acid-induced transformation which can be completely suppressed when base-washed glassware was used for the thermolysis.

Although the conversion of the cyclopropenyl-substituted oxazolinones to the pyridine ring system can be accommodated by the reaction sequence outlined in Scheme II, several other plausible routes were considered as likely alternatives. To aid in distinguishing among these pathways, we have examined the thermal behavior of a more extensively labeled system. Heating a sample of oxazolinone **17** at 150 °C for 24 h afforded a mixture of

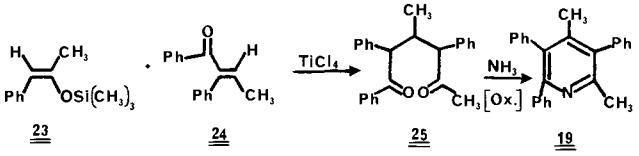


2,3-dimethyltriphenylpyridine (**18**) (45%), 2,4-dimethyltriphenylpyridine (**19**) (20%), and 2,5-dimethyltriphenylpyridine (**20**) (35%). Assignment of the various isomers was made by comparison with independently synthesized samples. The fact that certain types of nitriles are capable of acting as dienophiles in Diels–Alder reactions[32–37] suggested a method for synthesizing the 2,3-dimethyl-substituted pyridine **18**. One of the features of Diels–Alder reactions with nitriles, which have made them unattractive dienophiles, is the requirement of an extremely high reaction temperature for cycloaddition.[35] Thus, most simple aryl and alkyl nitriles cannot be used under "normal" reaction conditions. However, it has been found that ethyl cyanoformate will react with a variety of cyclic and acyclic dienes under fairly mild conditions.[38] Preparation of an authentic sample of 2,3-dimethyl-4,5,6-triphenylpyridine (**18**) was accomplished by allowing 2-methyl-3,4,5-triphenylcyclopentadiene (**21**) to undergo [4 + 2]



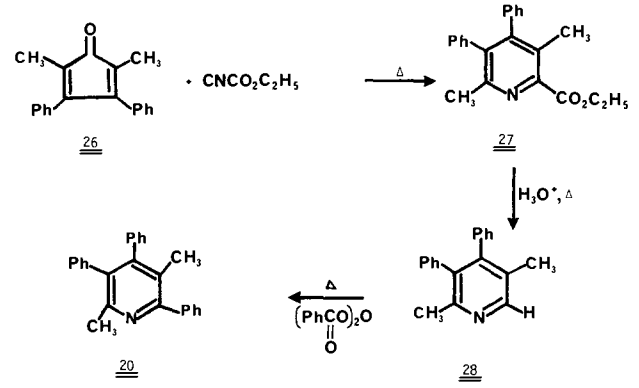
cycloaddition with ethyl cyanoformate. Reduction of the resulting cycloadduct with lithium aluminum hydride and then conversion of the alcohol to the chloride followed by treatment with zinc in acetic acid gave pyridine **18**.

The assignment of the 2,4-isomer was confirmed by comparison with an independently synthesized sample. Conjugate addition of 1-phenyl-2-(trimethylsiloxy)-1-propene (**23**) to 1,2-diphenyl-



2-buten-1-one (**24**) according to the method of Mukaiyama[39] gave 1,5-diketone **25**. Treatment of **25** with ammonia followed by oxidation afforded pyridine **19** in high yield.

The structure of the remaining pyridine was also confirmed by comparison with an authentic sample. Heating a sample of the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone (**26**) with ethyl cyanoformate gave rise to the expected Diels–Alder product. The resulting [4 + 2] cycloadduct **27** was converted to the corresponding acid which was thermally decarboxylated at 200 °C to give 2,5-dimethyl-3,4-diphenylpyridine (**28**). Treatment of this material with benzoyl peroxide in refluxing acetic acid gave the 2,5-substituted isomer **20** in 35% yield.[40,41]



In marked contrast to the thermal results, the photolysis of oxazolinone **17** gave rise to a rearranged Δ^2-oxazolinone **29** (80%) as well as a mixture of ring opened dienes (**30** and **31**) (20%). The two dienes were readily interconverted under the photolytic conditions employed. Heating Δ^2-oxazolinone **29** at 70 °C resulted in the regeneration of the thermodynamically more stable Δ^2-oxazolinone **17**. This conversion also occurred when a sample of **29** was subjected to thick-layer chromatography. A similar rearrangement took place when a sample of **29** was stirred in chloroform in the presence of *p*-toluenesulfonic acid. Attempts

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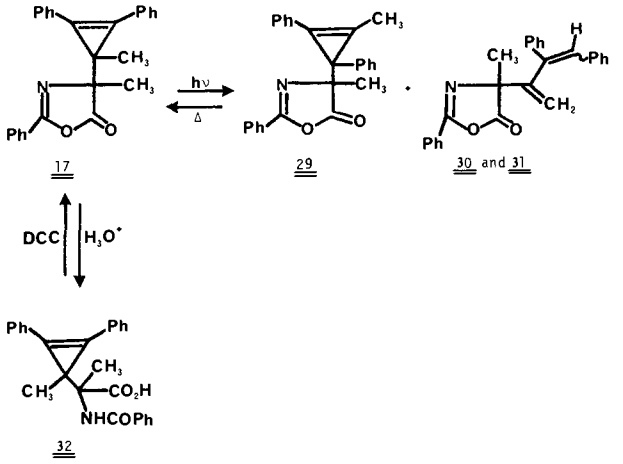
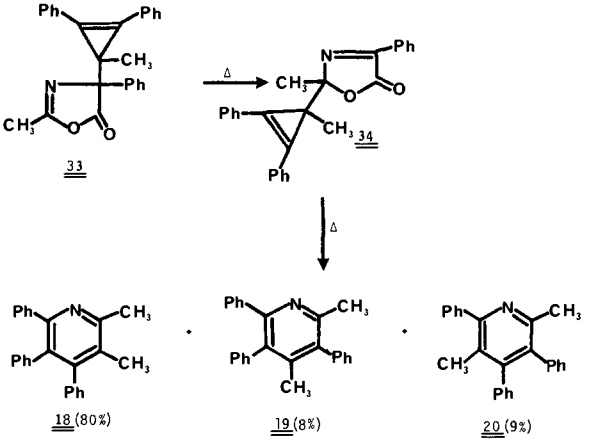


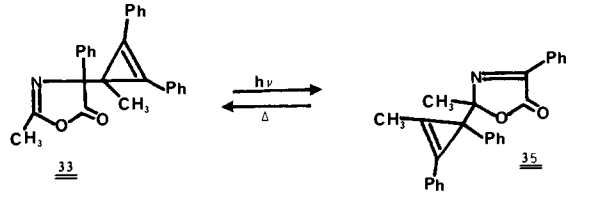
to purify a sample of **17**, obtained from the acid-induced rearrangement of **29**, by silica gel chromatography led to the formation of the ring-opened *N*-benzoyl amino acid **32**. This material could be readily converted back to **17** by treatment with dicyclohexylcarbodiimide.

We have also examined the thermal extrusion of carbon dioxide from the closely related Δ^2-oxazolinone **33**. Upon heating at 80



°C for 90 min, **33** was found to rearrange to the isomeric Δ^3-oxazolinone **34** in quantitative yield. Further heating of **34** at 170 °C for 25 h gave pyridines **18–20**. In this case, however, the ratio of the three dimethyl-substituted pyridines is substantially different from that encountered in the thermolysis of Δ^2-oxazolinone **17**.

In contrast to the plethora of compounds obtained from the thermolysis of **33**, photolysis of this material produced the unsymmetrical substituted Δ^3-oxazolinone **35** as the exclusive pho-

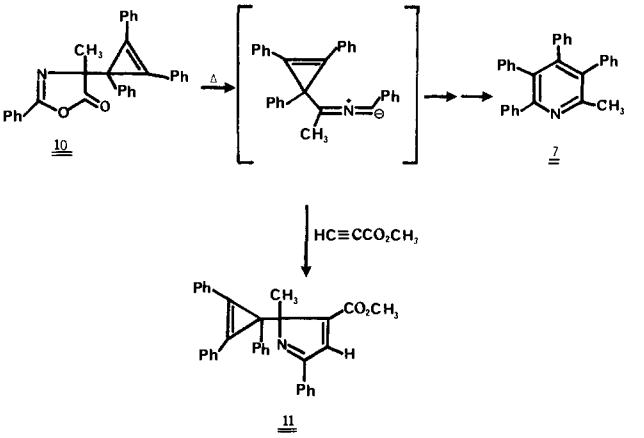


toproduct. Reorganization of the unsymmetrical cyclopropenyl-substituted Δ^3-oxazolinone **35** to the symmetrical Δ^2-isomer **33** occurred when **35** was stirred in acetonitrile at room temperature.

Discussion

Nitrile ylides belong to a class of 1,3-dipoles to which the general name nitrilium betaines has been given.[42] These reactive species have been known for over 20 years[43] and continue to elicit the interest of both experimental[44] and theoretical chemists.[45] 1,3-Dipolar cycloaddition of this class of 1,3-dipoles has led to the synthesis of a variety of interesting heterocyclic compounds.[46,47] Recently, it has been shown that intramolecular 1,1-cycloaddition of nitrile ylides can compete with the normal 1,3-addition when certain geometric restrictions are imposed.[48,49] In these cases, the reaction has been formulated in terms of the carbene form of the dipole.[45,49] Besides the Huisgen procedure which involves the elimination of hydrogen chloride from imidoyl chlorides,[50] other accesses to nitrile ylides include the photolysis of 2*H*-azirines[46,47] and the thermal elimination of carbon dioxide from oxazolinones.[21]

We believe that the thermal conversion of the cyclopropenyl-substituted oxazolinone to the substituted pyridine begins with a 1,3-cycloelimination of carbon dioxide yielding a nitrile ylide intermediate. Support for this contention comes from the isolation of 2*H*-pyrrole **11** when the thermolysis of a representative oxa-



zolinone (i.e., **10**) was carried out in the presence of methyl propiolate. The formation of **11** is most readily interpreted in terms of 1,3-dipolar cycloaddition of the initially generated nitrile ylide with the added dipolarophile.

Previous papers from this laboratory have established that allyl-substituted nitrile ylides undergo cycloaddition in a nonconcerted manner[51] by a process which bears a strong resemblance to the stepwise diradical mechanism suggested by Firestone to account for bimolecular 1,3-dipolar cycloadditions.[52] In a similar fashion, the stepwise cycloaddition of the nitrile ylide (**36**) derived from the thermolysis of oxazolinone **17** produces a bicyclobutyl zwitterion **37** which can either collapse to give azabenzvalene **38** or undergo rearrangement to the cyclobutenyl cation **39**. When the concepts of Closs and Pfeffer[53] are applied to the thermal rearrangement of azabenzvalene **38**, it can be seen that the 2,3-disubstituted pyridine **18** results from cleavage of the a–b and c–d bonds, while the 2,4-isomer **19** is derived from a similar cleavage of the a–c and b–d bonds. The cyclobutenyl cation **39** will give two different aza Dewar benzenes (**40** and **41**), which, in turn, will produce pyridines **18** and **20**. The ring expansion of **36** is undoubtedly facilitated by release of strain in the three-membered

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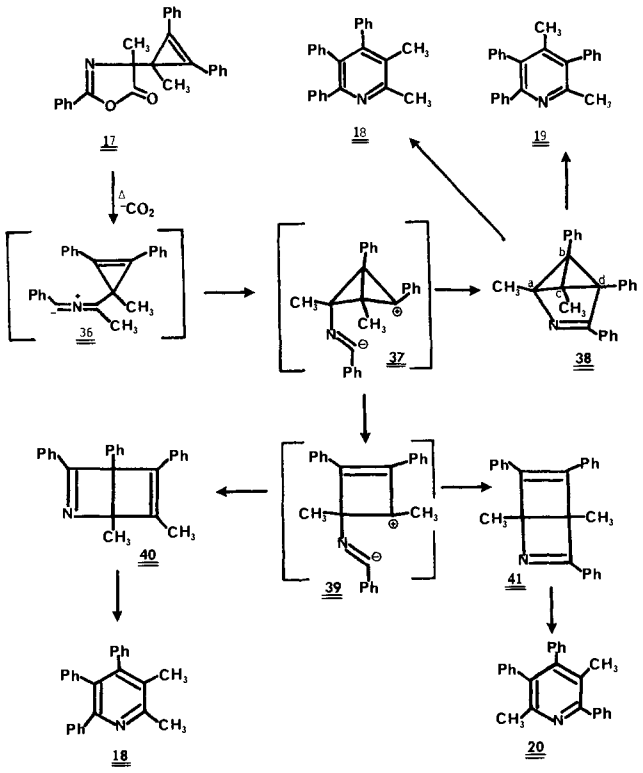
(51) Padwa, A.; Carlsen, P. H. J. *J. Am. Chem. Soc.* **1975**, *97*, 3862. Padwa, A.; Ku, A. *Ibid.* **1978**, *100*, 2181.

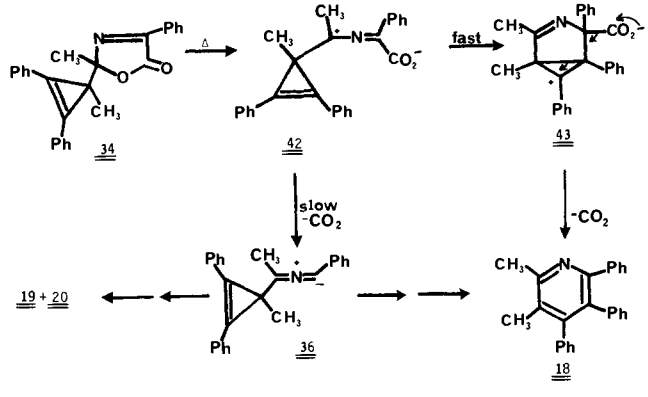
(52) Firestone, R. *J. Org. Chem.* **1968**, *33*, 2285; *Ibid.* **1972**, *37*, 2181; *J. Chem. Soc. A.* **1970**, 1570.

(53) Closs, G. L.; Pfeffer, P. E. *J. Am. Chem. Soc.* **1968**, *90*, 2452.



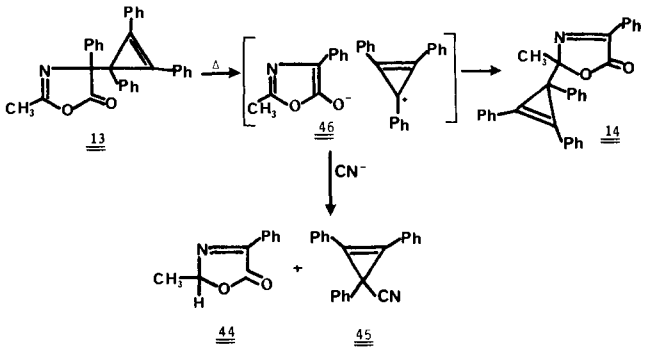
ring and is analogous to similar reactions reported by Breslow and co-workers.[54] It should be pointed out that classical forms of carbonium ions have been drawn for simplicity, although it is recognized that in all of them considerably more delocalization of charge is probable.[55]

The significant difference in product distribution formed in the thermolysis of oxazolinone **34** vs. that found with **17** indicates that this reaction does not proceed via simple loss of carbon dioxide. If this were the case, the distribution of pyridines (i.e., **18–20**) should be the same since both oxazolinones would give the same nitrile ylide intermediates (i.e., **36**). The preferential formation



of the 2,3-dimethyl-substituted isomer from oxazolinone **34** can be understood in terms of (1) opening of the Δ^3-oxazolinone ring to product zwitterion **42**, (2) cyclization of this species to azabicyclo[3.1.0]hexene **43**, and (3) simultaneous or stepwise extrusion of carbon dioxide from **43** to give pyridine **18**. Loss of CO_2 from the initial ring-opened intermediate **42** also occurs to produce nitrile ylide **36**, which ultimately affords pyridines **18–20**. A strong argument can be made that the cyclization of **42** to **43** is faster than loss of carbon dioxide. This is predicated on the fact that Δ^2-oxazolinones lose CO_2 at a much faster rate than the isomeric Δ^3-oxazolinone system.[56]

The thermal rearrangement of the Δ^2-oxazolinone to the Δ^3-isomer is an interesting reaction which merits some comment. The rate of reorganization of the Δ^2-isomer (e.g., **13**) to the Δ^3-isomer (e.g., **14**) 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 suggests 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 pair which subsequently collapses to the more stable product. The driving force for this reaction involves the creation of a more highly conjugated π-system in the Δ^3-isomer. Support for this mechanism comes from carrying out the thermolysis of **13** in the presence of potassium cyanide. Under these conditions the yield of **14** is substantially diminished and 3-cyanocyclopropene **45** and azlactone **44** were also isolated. This is consistent with the trapping of ion pair **46**. It should be pointed out that other examples of allylic migration of cyclopropenes which proceed through a dissociation–reassociation path are known in the literature and provide good analogy for the pathway outlined above.[57] The formation of oxazolinone **33** from the thermolysis of **35** can also be accommodated by the above mechanism. Breslow and coworkers had previously shown that alkyl groups stabilize cyclopropenyl cations more than phenyl groups.[58] This reversal of substituent effects was rationalized by assuming that the aromatic cyclopropenyl cation would not accept more electrons into its π system as required for assistance by a phenyl group. The cation can be stabilized by an inductive effect in which electron shifts occur within the σ bond. Such an effect is presumably responsible for the fact that nucleophilic attack on a diphenylalkyl-substituted cyclopropenyl cation occurs at the alkylated carbon atom.[59] The initially produced ion pair derived from **35** would be expected to react at the α-carbon atom of the oxazolinone ring since this atom represents the site of highest electron density. On further heating, the thermodynamically more favored Δ^3-oxazolinone **34** is eventually produced. A similar explanation accounts for the formation of **17** from the thermolysis of oxazolinone **29**.

Remaining for discussion are the photochemical reactions of the cyclopropenyl-substituted oxazolinone system. Singlet states of cyclopropenes generally react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinyl carbenes.[60] Thus, the formation of the indenyl-substituted oxazolinone **12** from the irradiation of **10** can readily be accounted for in terms of a transient vinyl carbene which cyclizes to an isoindene intermediate which subsequently undergoes a 1,5-sigmatropic shift to give the aromatic indene system.[61] In this case,

(54) Breslow, R.; Battiste, M. *J. Am. Chem. Soc.* **1960**, *82*, 3626. Breslow, R.; Lockhart, J.; Small, A. *Ibid.* **1962**, *84*, 2793.

(55) One of the reviewers has pointed out that another way of accounting for the product distribution is to assume a set of parallel reactions, i.e., **36** → **38** → **18** + **19** and **36** → **37** → **39** → **18** + **20**.

(56) Padwa, A.; Wetmore, S. I. *J. Am. Chem. Soc.* **1974**, *96*, 2414.

(57) Padwa, A.; Blacklock, T. J.; Cordova, D. M.; Loza, R. *J. Am. Chem. Soc.* **1980**, *102*, 5648.

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

(59) Johnson, R. W.; Widlanski, T.; Breslow, R. *Tetrahedron Lett.* **1976**, 4685.

(60) Padwa, A. *Org. Photochem.* **1979**, *4*, 261.

(61) Padwa, A.; Blacklock, T. J.; Getman, D.; Hatanaka, N.; Loza, R. *J. Org. Chem.* **1978**, *43*, 1481.

the incident light induces cleavage of the cyclopropene ring rather than extrusion of carbon dioxide. Yet another reaction undoubtedly resulting from a vinyl carbene intermediate is the formation of dienes **30** and **31** from the irradiation of oxazolinone **17**. These compounds can nicely be accommodated by a hydrogen shift from the initially generated vinyl carbene intermediate.[62] Systematic probing into the photoreactivity of a number of cyclopropene derivatives has led to the discovery that side chain fragmentation can compete with ring cleavage as a primary process when stable radicals are produced.[63] The formation of the unsymmetrical cyclopropenes (i.e., **29** and **35**) from the irradiation of oxazolinones **17** and **33** is worth noting. This reaction corresponds to an example of a singlet state reaction of a cyclopropene in which the three-membered ring has been retained.[63] A mechanism analogous to that accepted for the β-scission reaction of ketones[64] can readily account for the formation of the rearranged cyclopropenyl oxazolinones. It should be pointed out that the formation of the unsymmetrical cyclopropene from the radical pair is to be expected since the transition state prefers to localize the odd electron on the phenylated carbon of the cyclopropene ring.[59]

Experimental Section[65]

Preparation of 3-Methyl-2-phenyl-2-(triphenylcyclopropenyl)-2*H*-azirine (6). To a solution containing 5.4 mL of diisopropylamine in 80 mL of tetrahydrofuran was added 15 mL of a 2.5 M *n*-butyllithium solution at −78 °C. The mixture was stirred for 15 min at −78 °C and 30 min at 0 °C and was then cooled again to −78 °C. A solution of 6.3 g of phenylacetone *N,N*-dimethylhydrazone in 10 mL of tetrahydrofuran was added at −78 °C, and the solution was allowed to warm to 0 °C and was stirred for 3 h. This solution was added to a slurry of 10.8 g of triphenylcyclopropenyl perchlorate in 400 mL of tetrahydrofuran at −78 °C. The solution was allowed to warm to 0 °C, stirred overnight, diluted with water and extracted with ether. The ethereal solution was washed with water and dried over anhydrous sodium sulfate. After removal of the solvent, the orange oil was purified by silica gel chromatography to give 12.7 g of a mixture of (*syn*- and (*anti*-1,2,3-triphenylcyclopropenyl)phenylacetone *N,N*-dimethylhydrazone: IR (neat) 2985, 2881, 1828, 1715, 1490, 1504, 1451, 1380, 1227, 1161, 1081, 1028, 960, 838, 792, 777, 760, 717, 698, 691 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.97 and 1.71 (3 H, s), 2.24 (6 H, s), 6.37 and 5.07 (1 H, s), 6.9–7.9 (20 H, m); MS, *m/e* 442, 427, 398, 384, 366, 267 (base).

Anal. Calcd for $C_{32}H_{30}N_2$: C, 86.94; H, 6.83; N, 6.33. Found: C, 86.90; H, 6.79; N, 6.23.

A solution containing 12.7 g of the above (triphenylcyclopropenyl)-phenylacetone *N,N*-dimethylhydrazone and 10 g of methyl iodide in 10 mL of absolute ethanol was refluxed for 4 h. The solvent was removed under reduced pressure to give 16.7 g of a crude solid which was recrystallized from acetonitrile–ether. The colorless solid (12.6 g) obtained was assigned as (1,2,3-triphenylcyclopropenyl)phenylacetone *N,N,N*-trimethylhydrazonium iodide on the basis of the following data: mp 179–180 °C; IR (KBr) 2950, 1786, 1636, 1587, 1484, 1460, 1432, 1353, 1174, 1121, 1071, 1021, 939, 909, 813, 775, 768, 752, 714, 699, 693 cm^{-1}.

Anal. Calcd for $C_{33}H_{33}N_2I$: C, 67.80; H, 5.86; N, 4.79. Found: C, 67.73; H, 5.71; N, 4.74.

To a solution containing 5.84 g of (1,2,3-triphenylcyclopropenyl)-phenylacetone *N,N,N*-trimethylhydrazonium iodide in 750 mL of dry 2-propanol was added 100 mL of a 0.1 M sodium isopropoxide solution in 2-propanol. The mixture was stirred overnight at room temperature. The solvent was removed under reduced pressure and taken up with 50 mL of benzene. The inorganic precipitate that formed was removed by filtration and the benzene was removed under reduced pressure to give a light-brown solid which was recrystallized from benzene–hexane to give 3.2 g of azirine **6** as a colorless solid: mp 150–151 °C; IR (KBr) 2985, 1587, 1479, 1433, 1351, 1299, 1258, 1242, 1176, 1149, 1096, 1066, 1049, 1020, 998, 982, 934, 910, 849, 787, 775, 769, 753, 739, 709, 694, 685 cm^{-1}; UV (95% ethanol) 334 nm (16 800), 315 (20 700), 227 nm (31 500); NMR ($CDCl_3$, 60 MHz) δ 2.30 (3 H, s), 7.1–7.8 (20 H, m); MS, *m/e* 397, 356, 267, 186, 142, 84, 77 (base).

Anal. Calcd for $C_{30}H_{23}N$: C, 90.64; H, 5.83; N, 3.52. Found: C, 90.38; H, 5.87; N, 3.36.

Rearrangement of 3-Methyl-2-phenyl-2-(triphenylcyclopropenyl)-2*H*-azirine (6). A solution containing 100 mg of 3-methyl-2-phenyl-2-(triphenylcyclopropenyl)-2*H*-azirine (**6**) in 220 mL of benzene was irradiated for 30 min with a 450 Hanovia lamp equipped with a Pyrex filter. The solvent was removed under reduced pressure to leave behind a light brown solid which was recrystallized from benzene–hexane to give a crystalline solid, mp 160–161 °C, whose structure was assigned as 2-methyl-3,4,5,6-tetraphenylpyridine (**7**) by comparison with an authentic sample:[20] IR (KBr) 3012, 1957, 1919, 1811, 1605, 1580, 1536, 1490, 1441, 1397, 1224, 1181, 1155, 1091, 1074, 1030, 1013, 970, 915, 838, 821, 801, 774, 762, 741, 698 cm^{-1}; UV (cyclohexane) 243 nm (27 500), 295 nm (10 900); NMR ($CDCl_3$, 60 MHz) δ 2.47 (3 H, s), 6.8–7.3 (m, 20 H); MS, *m/e* 397, 396, 186, 146, 135, 131, 130, 129, 128, 199, 115, 105, 104, 103, 91, 77.

Anal. Calcd for $C_{30}H_{23}N$: C, 90.64; H, 5.83; N, 3.52. Found: C, 90.47; H, 5.87; N, 3.24.

The same product was also obtained by treating **6** with silver perchlorate in benzene or by refluxing **6** in toluene for 48 h.

Preparation of (Triphenylcyclopropenyl)propiophenone *N,N,N*-Trimethylhydrazonium Iodide. To a solution containing 4.2 mL of diisopropylamine in 90 mL of tetrahydrofuran was added 13.5 mL of a 2.5 M solution of *n*-butyllithium at 0 °C and the mixture was stirred for an additional 30 min. A solution of 5.3 g of propiophenone *N,N*-dimethylhydrazone in 60 mL of tetrahydrofuran was added to the above solution and the mixture was stirred for 2 h at 0 °C. This solution was added to a slurry of 10.8 g of triphenylcyclopropenyl perchlorate in 350 mL of tetrahydrofuran at 0 °C and the mixture was stirred for 12 h at 5 °C. Ether was added to the reaction mixture and the ethereal solution was washed with water and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residual oil (13 g) was recrystallized from hexane–benzene to give 8.5 g of the hydrazone as a solid: mp 144–145 °C; IR (KBr) 2994, 1602, 1575, 1495, 1466, 1443, 1357, 1305, 1277, 1193, 1151, 1095, 1021, 1014, 998, 971, 949, 912, 840, 801, 765, 721, 702, 688 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.10 (3 H, d, J = 7.4 Hz), 2.66 (6 H, s), 5.40 (1 H, q, J = 7.4 Hz), 6.6–7.6 (20 H, m); MS, *m/e* 398, 384, 365, 324, 267, 175, 160, 77.

Anal. Calcd for $C_{32}H_{30}N_2$: C, 86.94; H, 6.83; N, 6.33. Found: C, 86.79; H, 6.85; N, 6.35.

A solution containing 1.2 g of the above dimethylhydrazone and 4.0 g of methyl iodide was stirred at room temperature for 12 h. At the end of this time the excess methyl iodide was removed under reduced pressure and the solid material that was left was recrystallized from acetonitrile–ether to give a white solid, mp 138–139 °C, whose structure was assigned as triphenylcyclopropenylpropiophenone *N,N,N*-trimethylhydrazonium iodide on the basis of its spectral and analytical properties: IR (KBr) 2950, 1637, 1587, 1460, 1433, 1353, 1170, 1118, 1067, 1016, 941, 907, 807, 775, 767, 693 cm^{-1}.

Anal. Calcd for $C_{33}H_{33}N_2I$: C, 67.80; H, 5.86; N, 4.79. Found: C, 68.08; H, 5.78; N, 4.48.

Unfortunately, all attempts to convert this hydrazonium iodide salt to the corresponding azirine failed.

Preparation and Thermolysis of 4-Methyl-4-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-phenyl-Δ^2-oxazolin-5-one (10). A solution containing 8.0 mL of a 1.6 M solution of *n*-butyllithium in hexane was added to a stirred solution containing 1.40 g of diisopropylamine in 32 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 2.10 g of a solution of 4-methyl-2-phenyl-Δ^2-oxazolin-5-one[66] in 32 mL of tetrahydrofuran was added. After stirring at 0 °C for 2 h, the reaction mixture was transferred by syringe to a stirred suspension containing 4.40 g of triphenylcyclopropenyl perchlorate in 100 mL of dry tetrahydrofuran which had been cooled to −78 °C. The reaction mixture was allowed to warm to room temperature over a 4-h period. The mixture was quenched with water and concentrated under reduced pressure. The residue was taken up in ether, washed with water, and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using a 5% acetone–hexane mixture as the eluent. The major fraction contained 4.59 g of a crystalline solid, mp 162–163 °C, whose structure was assigned as 4-methyl-4-(1,2,3-triphenyl-2-cyclopropenyl)-2-phenyl-Δ^2-oxazolin-5-one (**10**) on the basis of the following data: IR (KBr) 1820, 1660, 1490, 1320, 1300, 1160,

(62) Pincock, J. A.; Morchat, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 7536.

(63) Padwa, A.; Blacklock, T. J.; Loza, R. *Tetrahedron Lett.* **1979**, 219.

(64) Turro, N. J. "Modern Molecular Photochemistry"; The Benjamin-Cummings Publishing Co.: Menlo Park, CA, 1978.

(65) 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 by using a Varian EM-390 spectrometer. Mass spectra were determined with a Finnegan 4000 mass spectrometer at an ionizing voltage of 70 eV.

(66) Padwa, A.; Akiba, M.; Cohen, L. A.; McDonald, J. G. *J. Org. Chem.* **1983**, *48*, 695.

1010, 910, 880, 760, 700, 690 cm^{-1}; UV (cyclohexane) 335, 318, 239 nm (ϵ 19 600, 25 800, 35 500); NMR ($CDCl_3$, 100 MHz) δ 1.29 (s, 3 H), 6.93–7.09 (m, 4 H), 7.25–7.65 (m, 10 H), 7.88–8.27 (m, 6 H); MS, *m/e* 397, 382, 381, 380, 320, 318.

Anal. Calcd for $C_{31}H_{23}NO_2$: C, 84.33; H, 5.25; N, 3.17. Found: C, 84.28; H, 5.27; N, 3.15.

Heating a sample of Δ^2-oxazolinone **10** at 150 °C in xylene for 24 h resulted in a quantitative yield of pyridine **7**.

Thermolysis of 4-Methyl-4-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-phenyl-Δ^2-oxazolin-5-one (10) in the Presence of Methyl Propiolate. A solution containing 309 mg of oxazolin-5-one (**10**), 1.21 g of methyl propiolate, 6 mL of *p*-xylene, and 6 drops of pyridine was heated at reflux for 26 h. Removal of the solvent under reduced pressure left a yellow oil which was chromatographed over silica using a 3% acetone–hexane mixture as the eluent. The major fraction isolated from the column was a white solid (102 mg), mp 159–160 °C, whose structure was assigned as 2-methyl-3-(1,2,3-triphenylcyclopropenyl)-3-carbomethoxy-5-phenyl-2*H*-pyrrole (**11**) on the basis of its spectral properties: IR (KBr) 2933, 1730, 1655, 1592, 1484, 1427, 1376, 1335, 1185, 1071, 1042, 1023, 970, 787, 766, 689 cm^{-1}; UV (cyclohexane) 335, 322, 227 nm (ϵ 15 000, 20 100, 26 600); NMR ($CDCl_3$, 100 MHz) δ 1.84 (s, 3 H), 2.76 (s, 3 H), 7.0–7.77 (m, 21 H).

Anal. Calcd for $C_{34}H_{27}NO_2$: C, 84.80; H, 5.65; N, 2.91. Found: C, 84.64; H, 5.69; N, 2.88.

Direct Irradiation of 4-Methyl-4-(1,2,3-triphenyl-2-cyclopropen-1-yl)-2-phenyl-Δ^2-oxazolin-5-one (10). A solution containing 300 mg of Δ^2-oxazolin-5-one (**10**) in 200 mL of benzene was irradiated in a Pyrex well for 75 min. The solvent was removed under reduced pressure leaving behind 280 mg (94%) of a pale yellow oil whose structure was assigned as 4-methyl-4-(1,2-diphenyl-3-indenyl)-2-phenyl-Δ^2-oxazolin-5-one (**12**) on the basis of the following spectral data: IR (neat) 1745, 1588, 1425, 1380, 1320, 1255, 1225, 1090, 915, 815, 610 cm^{-1}; UV (cyclohexane) 332, 316, 302, 228 nm (ϵ 7 700, 13 200, 11 600, 31 000); NMR ($CDCl_3$, 60 MHz) δ 1.84 (d, 3 H, J = 2.0 Hz), 4.66 (q, 1 H, J = 2.0 Hz), 6.75–7.87 (m, 19 H).

Anal. Calcd for $C_{31}H_{23}NO_2$: C, 84.33; H, 5.25; N, 3.17. Found: C, 84.38; H, 5.37; N, 3.09.

Preparation of 2,4-Diphenyl-4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (8). A solution containing 2.0 mL of a 1.6 M solution of *n*-butyllithium in hexane was added to 351 mg of diisopropylamine in 8 mL of tetrahydrofuran at 0 °C. The mixture was allowed to stir for 15 min and then a solution containing 712 mg of 2,4-diphenyl-Δ^2-oxazolin-5-one in 8 mL of tetrahydrofuran was added to the solution. 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. The mixture was stirred for 1 h at −78 °C and was then allowed to warm to room temperature over a 5-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 layer was dried and the solvent was removed under reduced pressure. The resulting residue was chromatographed on a silica gel column using a 5% acetone–hexane mixture as the eluent. The major fraction contained 937 mg (71%) of a crystalline solid, mp 127–128 °C, whose structure was assigned as 2,4-diphenyl-4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (**8**): IR (KBr) 1786, 1634, 1471, 1431, 1311, 1282, 1133, 1050, 936, 907, 866, 754, 684 cm^{-1}; UV (cyclohexane) 334, 316, 237 nm (ϵ 22 000, 27 000, 28 000); NMR ($CDCl_3$, 60 MHz) δ 1.46 (s, 3 H), 6.94–7.10 (m, 3 H), 7.19–7.52 (m, 9 H), 7.53–7.85 (m, 6 H), 8.01–8.16 (m, 2 H).

Anal. Calcd for $C_{31}H_{23}NO_2$: C, 84.33; H, 5.25; N, 3.17. Found: C, 84.26; H, 5.31; N, 3.09.

Thermolysis of 2,4-Diphenyl-4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-Δ^2-oxazolin-5-one (8). A solution containing 135 mg of oxazolinone **8** in 3 mL of toluene was heated at reflux for 20 h. The solvent was removed under reduced pressure to give a light yellow solid which was recrystallized from ethyl acetate–hexane to give 99 mg (88%) of a crystalline solid, mp 185–186 °C, whose structure was assigned as 3-methyl-2,4,5,6-tetraphenylpyridine (**9**) on the basis of its spectral properties and by comparison with an independently synthesized sample:[31] IR (KBr) 3070, 1510, 1465, 1440, 1390, 1260, 1065, 920, 900, 730, 690 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.17 (s, 3 H), 6.83–7.83 (m, 20 H).

Anal. Calcd for $C_{30}H_{23}N$: C, 90.64; H, 5.83; N, 3.52. Found: C, 90.58; H, 5.71; N, 3.46.

Thermolysis of 2-Methyl-2-(1,2,3-triphenyl-2-cyclopropen-1-yl)-4-phenyl-Δ^3-oxazolin-5-one (14). A solution containing 300 mg of Δ^3-oxazolin-5-one (**14**)[66] in 10 mL of toluene was heated at 117 °C. The progress of the reaction was monitored by NMR spectroscopy. After heating for 15 h, the starting oxazolinone had completely disappeared and two new compounds were present in the crude reaction mixture. The minor component (22%) was identified as 2-methyl-3,4,5,6-tetraphenylpyridine (**7**) by comparison with an authentic sample.[20] The major compound (78%) showed signals at δ 4.61 (s, 1 H), 4.67 (s, 1 H), and 8.20 (s, 1 H) in addition to the aromatic protons at 7.0–8.0 (m, 20 H). Allowing the solution to stir with a small amount of water caused these signals to disappear. Two new compounds were produced and were subsequently shown to be benzaldehyde and 1,2,3-triphenyl-3-acetylcyclopropene (**16**). Chromatography of the crude reaction mixture gave a pure sample of 2-methyl-3,4,5,6-tetraphenylpyridine (**7**), mp 160–161 °C (lit.[20] 161 °C), as well as 1,2,3-triphenyl-3-acetylcyclopropene (**16**): mp 140–141 °C; IR (KBr) 1683, 1603, 1492, 1405, 1384 cm^{-1}; UV (95% ethanol) 228, 285, 297, 327, 337 nm (ϵ 11 200, 15 600, 19 400, 20 100, 19 900); NMR ($CDCl_3$, 100 MHz) δ 2.02 (s, 3 H), 7.36–7.90 (m, 15 H); MS, *m/e* 310 (M^+), 267 (base).

Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.98; H, 6.10.

The structure of this material was further verified by an independent synthesis.[67]

Thermolysis of 4-Methyl-4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-phenyl-Δ^2-oxazolin-5-one (17). A solution containing 455 mg of oxazolin-5-one (**17**)[66] in 5 mL of a 9:1 benzene–pyridine mixture was heated in a sealed tube at 146 °C for 34 h. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using a 3% acetone–hexane mixture as the eluent. The first fraction isolated from the column contained 90 mg (20%) of a crystalline solid, mp 125–126 °C, whose structure was assigned as 2,4-dimethyl-3,5,6-triphenylpyridine (**19**) on the basis of its spectral properties and by comparison with an independently synthesized sample: IR (KBr) 3016, 1599, 1537, 1491, 1439, 1397, 1066, 1026, 1003, 776, 751, 686 cm^{-1}; UV (cyclohexane) 282 nm (ϵ 9060); NMR ($CDCl_3$, 60 MHz) δ 1.82 (s, 3 H), 2.36 (s, 3 H), 6.85–8.1 (m, 15 H); MS, *m/e* 335 (M^+), 334, 205.

Anal. Calcd for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18. Found: C, 89.62; H, 6.40; N, 4.16.

The second fraction isolated from the column contained 202 mg (45%) of a crystalline solid, mp 119–120 °C, whose structure was assigned as 2,3-dimethyl-4,5,6-triphenylpyridine (**18**) on the basis of its spectral properties and by comparison with an independently synthesized sample: IR (KBr) 1534, 1479, 1425, 1387, 1068, 1027, 766, 694 cm^{-1}; UV (cyclohexane) 286, 235 nm (ϵ 9 100, 21 800); NMR ($CDCl_3$, 60 MHz) δ 2.06 (s, 3 H), 2.65 (s, 3 H), 6.60–7.38 (m, 15 H); MS, *m/e* 335 (M^+), 334 (base), 205.

Anal. Calcd for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18. Found: C, 89.49; H, 6.36; N, 4.17.

The last fraction isolated from the chromatography column contained 155 mg (35%) of a crystalline solid, mp 175–176 °C, whose structure was identified as 2,5-dimethyl-3,4,6-triphenylpyridine (**20**) on the basis of its spectral properties and by comparison with an independently synthesized sample: IR (KBr) 1538, 1479, 1435, 1379, 1070, 1022, 799, 778, 760, 746, 700 cm^{-1}; UV (cyclohexane) 290, 287, 238 nm (ϵ 20 800, 9 000, 6 800); NMR ($CDCl_3$, 60 MHz) δ 1.99 (s, 3 H), 2.36 (s, 3 H), 6.84–7.60 (m, 15 H); MS, *m/e* 335 (M^+), 334, 333, 319, 205.

Anal. Calcd for $C_{25}H_{21}N$: C, 89.51; H, 6.31; N, 4.18. Found: C, 89.42; H, 6.38; N, 4.16.

Independent Synthesis of 2,3-Dimethyl-4,5,6-triphenylpyridine (18). A mixture containing 3.22 g of 2-methyl-3,4,5-triphenylcyclopentadienone (**21**)[68] and 3.96 g of ethyl cyanoformate was heated with stirring at 190 °C for 16 h. The crude reaction mixutre was chromatographed on a silica gel column eluting with a 5% acetone–hexane mixture. The major component isolated from the column contained 3.02 g (77%) of a white solid, mp 132–133 °C, whose structure was assigned as 2-carboethoxy-3-methyl-4,5,6-triphenylpyridine (**22**) on the basis of its spectral properties: IR (KBr) 1724, 1441, 1395, 1362, 1337, 1266, 1242, 1212, 1098, 1076, 1032, 1015, 760, 729, 702 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.39 (t, 3 H, J = 7.0 Hz), 2.21 (s, 3 H), 4.41 (q, 2 H, J = 7.0 Hz), 6.67–7.35 (m, 15 H); MS, *m/e* 393 (M^+), 392, 322, 321 (base), 320, 319, 318.

Anal. Calcd for $C_{27}H_{23}NO_2$: C, 82.42; H, 5.89; N, 3.56. Found: C, 82.33; H, 5.95; N, 3.55.

The minor component isolated from the column contained 310 mg (8%) of a white solid, mp 131–132 °C, whose structure is assigned as 2-carboethoxy-6-methyl-3,4,5-triphenylpyridine: IR (KBr) 1721, 1393, 1323, 1239, 1199, 1020, 767, 732, 702 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 0.92 (t, 3 H, J = 7.0 Hz), 2.44 (s, 3 H), 4.05 (q, 2 H, J = 7.0 Hz), 6.54–7.28 (m, 15 H); MS, *m/e* 393 (M^+), 349, 321, 320, 252, 224, 205, 111, 58.

A solution containing 1.57 g of 2-carboethoxy-3-methyl-4,5,6-triphenylpyridine (**22**) in 50 mL of ether was added to a stirred suspension

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containing 304 mg of lithium aluminum hydride in 50 mL of ether at 0 °C. The mixture was heated at reflux for 1 h and was then quenched with water. The ether layer was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure to leave behind 1.60 g of a yellow oil. This material was chromatographed on a silica gel column eluting with a 5% acetone–hexane mixture. The major component isolated from the column contained 1.14 g of a white solid, mp 129–130 °C, whose structure was assigned as 2-hydroxymethyl-3-methyl-4,5,6-triphenylpyridine: IR (KBr) 3135, 1536, 1433, 1387, 1035, 767, 696 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.96 (s, 3 H), 4.75 (s, 2 H), 5.15 (br s, 1 H, exchanged with D_2O), 6.65–7.38 (m, 15 H).

Anal. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02; N, 3.99. Found: C, 85.38; H, 6.05; N, 3.97.

A solution containing 281 mg of the above compound in 2 mL of thionyl chloride was heated at reflux for 1 h. The excess thionyl chloride was removed under reduced pressure and the residue was neutralized with aqueous sodium carbonate and extracted with ether. The ether was dried over magnesium sulfate to leave behind a light oil whose NMR showed a singlet at δ 2.20 (3 H) and a singlet at 4.81 (2 H). This material was taken up in 2 mL of glacial acetic acid and 140 mg of zinc dust was added. The reaction mixture was heated at 100 °C for 6 h. The solution was cooled, filtered, and concentrated under reduced pressure. The residue was made alkaline with a 1% sodium hydroxide solution and was extracted with ether. The combined ether extracts were washed with water and dried over magnesium sulfate. Removal of the solvent left 198 mg (74%) of a crystalline solid, mp 119–120 °C, whose spectral properties were identical with the major pyridine isomer obtained from the thermolysis of oxazolin-5-one **17**.

Independent Synthesis of 2,4-Dimethyl-3,5,6-triphenylpyridine (19). An authentic sample of 2,4-dimethyl-3,5,6-ttriphenylpyridine (**19**) was prepared by treating 1,2,4-triphenyl-3-methylhexane-1,5-dione (**25**) with ammonia. The desired hexane-1,5-dione was prepared by the conjugated addition of 1-phenyl-2-(trimethylsiloxy)-1-propene (**23**) to 1,2-diphenyl-2-buten-1-one. A sample of the above conjugated ketone was prepared by the dehydration of 1-benzoyl-1-phenylpropan-1-ol.[69] To a mixture containing 8.58 g of ethyl iodide and 10.61 g of benzoin in 100 mL of dimethyl sulfoxide was added 22 mL of a 10% aqueous sodium hydroxide solution. The solution was allowed to stir at 25 °C for 12 h and was then quenched with 40 mL of water. The reaction mixture was extracted with ether and the ethereal layer was washed with water and then dried over magnesium sulfate. Removal of the solvent left 11.65 g (97%) of an oil whose NMR indicated it to be 1-benzoyl-1-phenylpropan-1-ol: ($CDCl_3$, 60 MHz) δ 0.80 (t, 3 H, J = 7.0 Hz), 2.30 (*q*, 2 H, J = 7.0 Hz), 6.93–8.09 (m, 10 H).

A 7.38-g sample of the above alcohol in 74 mL of formic acid was heated at reflux for 4 h. At the end of this time the mixture was diluted with 40 mL of water and extracted with ether. The ether layer was washed with water and concentrated under reduced pressure. The resulting oil was passed through an alumina column using a 0.5% ethyl acetate–pentane mixture as the eluent to give 5.4 g of a 2:1 mixture of the *E* and *Z* isomers of 1,2-diphenyl-2-buten-1-one (**24**): NMR ($CDCl_3$, 60 MHz) *E* isomer δ 1.73 (d, 3 H, J = 7.0 Hz), 6.46 (g, 1 H, J = 7.0 Hz), 6.95–8.16 (m, 10 H); *Z* isomer δ 1.65 (d, 3 H, J = 7.0 Hz), 6.21 (q, 1 H, J = 7.0 Hz), 6.95–8.16 (m, 10 H).

A sample of 1-phenyl-2-(trimethylsiloxy)-1-propene (**23**) was conveniently prepared from phenylacetone.[70] A mixture containing 6.32 g of phenylacetone, 1.90 g of sodium hydride, and 40 mL of 1,2-dimethoxyethane was stirred for 3.5 h and was then allowed to stand for an additional 14 h. The supernatant liquid was transferred to a solution containing 7.68 g of trimethylsilyl chloride in 50 mL of 1,2-dimethoxyethane at 0 °C. After stirring for 1 h at 25 °C, 80 mL of pentane was added to the solution. The solution was washed with a saturated sodium bicarbonate solution followed by water and was then dried over magnesium sulfate. The solvent was removed under reduced pressure and the resulting residue was distilled at 45–55 °C (0.15 mm) to give 1-phenyl-2-(trimethylsiloxy)-1-pentene (**23**) (57%) as a clear liquid: NMR ($CDCl_3$, 60 MHz) δ 0.01 (s, 9 H), 5.20 (s, 3 H), 6.81–7.48 (m, 5 H), 8.24 (s, 1 H).

A solution containing 800 mg of 1-phenyl-2-(trimethylsiloxy)-1-propene (**23**) in 1.5 mL of methylene chloride was added to a stirred solution containing 689 mg of 1,2-diphenyl-2-buten-1-one (**24**) and 0.39 mL of titanium tetrachloride in 4.5 mL of methylene chloride at −78 °C. The mixture was stirred at −78 °C for 1 h and was then poured into a 5% aqueous sodium carbonate solution. The aqueous phase was extracted with methylene chloride and the combined extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure to give 1.23 g of a mixture of diastereomers of 1,2,4-triphenyl-3-methylhexane-1,5-dione (**25**): IR (KBr) 3170, 3120, 3070, 3020, 2970, 1820, 1790, 1710, 1690, 1600, 1560, 1460, 1380, 1310, 1280, 1110, 860, 800 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 0.67 (d, 3 H, J = 7.0 Hz), 0.85 (d, 3 H, J = 7.0 Hz), 1.73 (s, 3 H), 2.07 (s, 3 H), 3.08–3.46 (m, 1 H), 3.66 (d, 1 H, J = 5.0 Hz), 3.76 (d, 1 H, J = 5.0 Hz), 4.48 (d, 1 H, J = 8.0 Hz), 4.65 (d, 1 H, J = 8.0 Hz), 6.93–8.07 (m, 15 H).

A solution containing 150 mg of 1,2,4-triphenyl-3-methylhexane-1,5-dione (**25**) and 20 mg of ammonium bromide in 5 mL of alcohol was saturated with ammonia at 0 °C. The reaction mixture was stirred at 25 °C for 48 h. The solvent was removed under reduced pressure and the crude residue was taken up in ether, washed with water, and dried over magnesium sulfate. The ether was removed under reduced pressure to give 130 mg of a 2,4-dimethyl-3,5,6-triphenylpyridine (**19**), mp 125–126 °C, whose spectral properties were identical with a sample of **19** obtained from the thermolysis of oxazolin-5-one **17**.

Independent Synthesis of 2,5-Dimethyl-3,4,6-Triphenylpyridine (20). A mixture containing 2.60 g of the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone[71] and 3.96 g of ethyl cyanoformate was heated under a nitrogen atmosphere at 175 °C for 16 h. The crude reaction mixture was chromatographed on a silica gel column using a 5% acetone–hexane mixture as the eluent. The major component isolated from the column contained 2.47 g (75%) of a crystalline solid, mp 108–109 °C, whose structure was assigned as 2-carboethoxy-3,6-dimethyl-4,5-diphenylpyridine (**27**) on the basis of its spectral properties: IR (KBr) 1709, 1435, 1397, 1325, 1271, 1238, 1098, 1070, 1015, 766, 742, 701 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 1.42 (t, 3 H, J = 7.0 Hz), 2.15 (s, 3 H), 2.34 (s, 3 H), 4.44 (q, 2 H, J = 7.0 Hz), 6.65–7.30 (m, 10 H); MS, m/e 331 (M^+), 330, 287, 259 (base), 258, 256.

Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.73; H, 6.39; N, 4.23. Found: C, 79.65; H, 6.40; N, 4.22.

A mixture containing 1.33 g of the above pyridine and 240 mg of sodium hydroxide in 5 mL of water and 2 mL of ethanol was heated at reflux for 30 min. The reaction mixture was diluted with 10 mL of water and acidified with a 1% hydrochloric acid solution. The aqueous layer was extracted with methylene chloride and the organic solution was washed with water and dried over magnesium sulfate. Removal of the solvent left a crude solid which was recrystallized from ethyl acetate-hexane to give 1.21 g of 3,6-dimethyl-4,5-diphenylpicolinic acid: mp 186–187 °C; IR (KBnr) 3135–2665, 1750, 1420, 1381, 1346, 1089, 1068, 1034, 958, 820, 762, 697 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.37 (br s, 3 H), 2.47 (br s, 3 H), 6.78–7.31 (m, 10 H), 11.6 (s, 1 H).

Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.65; N, 4.62. Found: C, 79.19; H, 5.68; N, 4.62.

A 607-mg sample of the above acid was heated in the melt at 200 °C for 1 h. The resulting yellow residue was chromatographed on a silica gel column using a 5% acetone–hexane mixture as the eluent. The major fraction contained 482 mg (93%) of 2,5-dimethyl-3,4-diphenylpyridine (**28**) as a crystalline solid, mp 114–115 °C; IR (KBr) 1548, 1422, 1376, 1063, 1022, 917, 907, 763, 733, 702 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 2.02 (s, 3 H), 2.30 (br s, 3 H), 6.72–7.24 (m, 10 H), 8.35 (br s, 1 H).

Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.99; H, 6.62; N, 5.39.

A mixture containing 259 mg of the above pyridine, 727 mg of benzoyl peroxide, and 2 mL of glacial acetic acid was heated at reflux for 1 h. The reaction mixture was poured into a 5% sodium hydroxide solution and extracted with benzene. The combined benzene extracts were washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column using a 5% acetone–hexane mixture as the eluent. The major fraction was unreacted 2,5-dimethyl-3,4-diphenylpyridine. The minor component present in the mixture (28%) was a colorless solid, mp 173–174 °C, which was identical in every detail with the 2,5-dimethyl-substituted isomer **20** prepared from the thermolysis of oxazolinone **17**.

Direct Irradiation of 4-Methyl-4-(1-methyl-2,3-diphenyl-2-cyclopropen-1-yl)-2-phenyl-Δ^2-oxazolin-5-one (17). A solution containing 300 mg of **17** in 250 mL of benzene was irradiated in a Pyrex photolysis well for 2 h. Removal of the solvent under reduced pressure left a crude residue which was subjected to silica gel chromatography using a 3% acetone–hexane mixture as the eluent. The major component isolated contained 240 mg of 2-phenyl-4-methyl-4-(1,3-diphenyl-2-methyl-2-cyclopropene-1-yl)-Δ^2-oxazolinone (**29**) (80%).[66] The other component isolated was shown to consist of a 1:1 mixture of *cis*-**30** and *trans*-4-methyl-4-(1,2-diphenyl-1,3-butadien-3-yl)-2-phenyl-Δ^2-oxazolin-5-one (**31**). The cis isomer was fractionally crystallized from the trans isomer and showed the following characteristics: mp 114–115 °C; IR (KBr) 3065, 3025, 1820, 1655, 1490, 1445, 1315, 1290, 1155, 1095, 1070, 915,

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875, 755, 740, 685 cm^{-1}; UV (cyclohexane) 278, 247 nm (ϵ 18 350, 24 000); NMR ($CDCl_3$, 100 MHz) δ 1.72 (s, 3 H), 5.50 (s, 1 H), 5.81 (s, 1 H), 6.76 (s, 1 H), 7.21–7.95 (m, 15 H).

Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.18; H, 5.26; N, 3.41.

The trans isomer (**31**) was purified by thick-layer chromatography using a 3% acetone–hexane mixture as the eluent to give a crystalline solid: mp 89–90 °C; IR (KBr) 1820, 1805, 1645, 1480, 1445, 1375, 1310, 1280, 1150, 1000, 905, 860, 680 cm^{-1}; UV (cyclohexane) 275, 234 nm (ϵ 14 500, 27 800); NMR ($CDCl_3$, 100 MHz) δ 1.65 (s, 3 H), 5.66 (s, 2 H), 6.76 (s, 1 H), 6.85–7.82 (m, 15 H).

Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.30; H, 5.58; N, 3.69. Found: C, 82.07; H, 5.35; N, 3.38.

The two butadienyl-substituted oxazolinones were interconverted by heating the cis isomer (**30**) in benzene with a trace of iodine.

Thermal- and Acid-Catalyzed Rearrangement of 4-Methyl-4-(2-methyl-1,3-diphenyl-2-cyclopropen-1-yl)-2-phenyl-Δ^2-oxazolin-5-one (29). A solution containing 39 mg of oxazolinone **29** in 0.5 mL of a 10% pyridine–benzene solution was heated in a sealed NMR tube at 70 °C for 168 h. At the end of this time the unsymmetric oxazolinone **29** had been completely converted to the corresponding symmetrical oxazolinone **17**. A similar rearrangement occurred when oxazolinone **29** was chromatographed on silica gel. Thus a 43-mg sample of **29** was predominntly converted to the symmetrical oxazolinone **17** on chromatography using a 3% acetone–hexane mixture as the eluent. A similar rearrangement occurred on stirring a sample of **29** in chloroform in the presence of *p*-toluenesulfonic acid. After stirring for 18 h, a 200 mg sample of **29** in 6 mL of chloroform was poured into 3 mL of water. The aqueous mixture was taken up in ether, washed with water, and dried over magnesium sulfate. Removal of the solvent left 160 mg (76%) of a yellow oil which was recrystallized from a 3% acetone–hexane mixture to give 150 mg of a white solid, mp 151–152 °C, whose structure was assigned as 1-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)-*N*-benzoylglycine (**32**) on the basis of the following data: IR (KBr) 3435, 3035, 2600, 1740, 1665, 1635, 1580, 1500, 1480, 1440, 1380, 1290, 1255, 1230, 1170, 1135, 1020, 895, 830, 755, 730, 680 cm^{-1}; UV (cyclohexane) 335, 317, 228 nm (ϵ 13 020, 17 950, 25 400); NMR ($CDCl_3$, 60 MHz) δ 1.64 (s, 3 H), 1.93 (s, 3 H), 6.55 (s, 1 H), 6.87–8.05 (m, 15 H).

Anal. Calcd for $C_{26}H_{23}NO_2$: C, 78.57; H, 5.83; N, 3.52. Found: C, 78.30; H, 5.90; N, 3.49.

This same material could also be prepared in 64% yield by heating a sample of oxazolin-5-one **32** in a 5:1 acetone water mixture at 80 °C for 18 h. Support for the structure of benzoylglycine **32** was obtained by its conversion to oxazolin-5-one **17**. A solution containing 72 mg of **32**, 37 mg of dicyclohexylcarbodiimide, and a trace of trifluoroacetic acid was heated at reflux in benzene for 46 h. The solvent was removed under reduced pressure and the resulting residue was shown to consist of oxazolin-5-one **17**.

Thermolysis of 4-Phenyl-4-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)-2-methyl-Δ^2-oxazolin-5-one (33). A solution containing 47 mg of oxazolin-5-one **33**[66] in 0.5 mL of a 10% pyridine–benzene solution was heated at 138 °C in a sealed tube for 12 h. At the end of this time the NMR spectrum showed the presence of 2,3-dimethyl-4,5,6-triphenylpyridine (**18**) (80%), 2,4-dimethyl-3,5,6-triphenylpyridine (**19**) (8%), and 2,5-dimethyl-3,4-triphenylpyridine (**20**) (9%). These structures were verified by comparison with authentic samples of the variously substituted dimethyltriphenylpyridines. Chromatography of the crude residue produced pure samples of pyridine which were identical in all details with the authentic samples.

When a solution of 100 mg of oxazolinone **33** in 2.0 mL of a 10% pyridine–benzene mixture was heated in a sealed tube at 80 °C for only 90 min, a new isomer was formed prior to the formation of the pyridines. 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 major 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 (**34**) 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, 338 nm (ϵ 17 800, 27 600, and 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, and 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.

Further heating of this material in a 10% pyridine–benzene solution at 138 °C in a sealed tube for 12 h produced a mixture of dimethyltriphenyl-substituted pyridines **18**, **19**, and **20** in yields of 80%, 8%, and 9%, respectively. The structures of the pyridines were verified by comparison with authentic samples.

Direct Irradiation of 4-Phenyl-4-(2,3-diphenyl-1-methyl-2-cyclopropen-1-yl)-2-methyl-Δ^2-oxazolin-5-one (33). A solution containing 110 mg of Δ^2-oxazolinone **33** in 200 mL of benzene was irradiated through a Pyrex well with a 450-W Hanovia lamp for 165 min. The solvent was removed under reduced pressure and the resulting yellow residue was chromatographed on a silica gel column using a mixture of triethylamine–acetone–hexane as the eluent. The first compound isolated from the column contained unreacted starting material (67%). The second component was a very sensitive oil which was found to rearrange back to oxazolinone **33** on standing at room temperature. This material is assigned the structure of 2-methyl-2-(1,3-diphenyl-2-methyl-2-cyclopropen-1-yl)-4-phenyl-Δ^3-oxazolin-5-one (**35**) on the basis of the following data: IR (neat) 2930, 2875, 1770, 1610, 1490, 1445, 1210, 1068, 905, 750, 680 cm^{-1}; UV (cyclohexane) 265, 238, 213 nm (ϵ 17 500, 10 400, 22 100); NMR ($CDCl_3$, 100 MHz) δ 1.40 (s, 3 H), 2.20 (s, 3 H), 7.03–7.83 (m, 15 H).

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.

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