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Studies Dealing with the Aza-Claisen Rearrangement of 2-Allyloxy-Substituted Oxazoles

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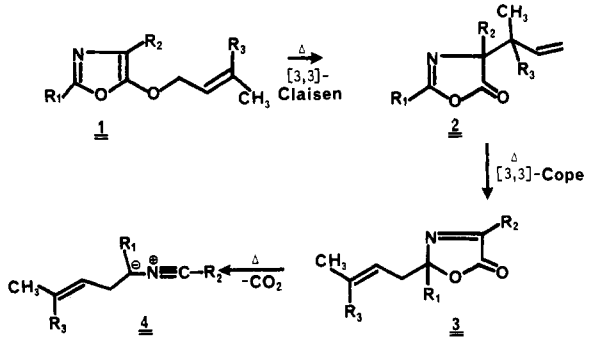
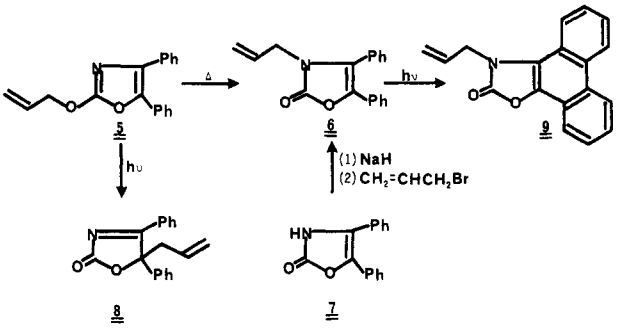
The scope of the thermal [3,3]-sigmatropic rearrangement of a number of 2-allyloxy-substituted 4,5-diphenyloxazoles has been examined. These systems undergo a facile aza-Claisen rearrangement to give 3-allyl-substituted 4,5-diphenyl-4-oxazolin-2-ones. In contrast to the thermal results, irradiation of the 2-allyloxy- or benzyloxy-substituted oxazole gave rise to a mixture of 3- and 5-substituted oxazolinones. The photolysis proceeds via C–O bond scission to generate a radical pair which subsequently recombines to produce the mixture of oxazolinones. A series of related oxazoles was prepared in which the heterocyclic ring and the π bond are connected by an alkoxy side chain. All attempts to induce an intramolecular Diels–Alder reaction failed. The only product that could be obtained corresponds to that derived from an intramolecular ene reaction. The excited-state behavior of several 2- and 5-allyloxy-substituted oxazoles was also studied. The rationale for the difference in thermal and photochemical behavior is discussed.

The Cope and Claisen rearrangements have found wide application in the synthesis of complex molecular systems.[1-3] The Claisen rearrangement, which transforms allyl vinyl ethers into γ,δ-unsaturated carbonyl compounds, has proven exceptionally useful as a general synthetic method due to its adaptability to a wide range of structural and functional variations. Although [3,3]-sigmatropic rearrangement of systems in which the vinyl moiety is incorporated into a benzene ring are well-known, analogous reactions of related heterocyclic systems have not been as well studied.[4] The tandem Claisen–Cope rearrangement[2] of a 5-allyloxy-substituted oxazole followed by carbon dioxide extrusion from the resulting Δ^3-oxazolinone systems (**3**) represents a particularly attractive method for



generating allyl-substituted nitrile ylides **4**.[5-10] The development of new methods for the formation of 1,3-dipoles under mild conditions has been a major objective of our work in the field of 1,3-dipolar cycloaddition chemistry.[11] As a result of our interest in this area, we initiated a study

Scheme I



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(2) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.
(3) Bennett, G. B. *Synthesis* **1977**, 589.
(4) Padwa, A.; Akiba, M.; Cohen, L. A.; MacDonald, J. G. *Tetrahedron Lett.* **1981**, *22*, 2435.
(5) Engel, N.; Kubel, B.; Steglich, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 394.
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(7) Fischer, J.; Steglich, W. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 167.
(8) Engel, N.; Fischer, J.; Steglich, W. *J. Chem. Res. Synop.* **1977**, 162.
(9) Steglich, W. *Fortschr. Chem. Forsch.* **1969**, *12*, 77.
(10) Hofle, G.; Steglich, W. *Chem. Ber.* **1971**, *104*, 1408.
(11) Padwa, A.; Caruso, T.; Nahm, S. *J. Org. Chem.* **1980**, *45*, 4065.

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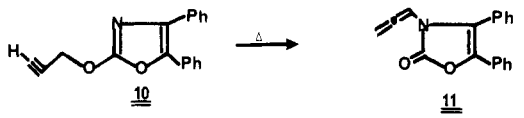
to explore the scope and applications of the Claisen rearrangement of a series of oxazoles in order to determine whether this method could be used to generate a heterocyclic ring system which would undergo further loss of carbon dioxide. If this scheme could be reduced to practice, a ready route to a variety of reactive heterocyclic intermediates would become available.

Results and Discussion

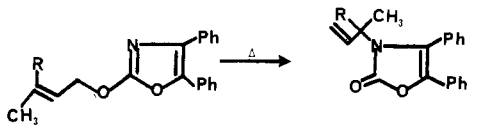
As our first model we chose to investigate the chemistry of a series of 2-allyloxy-substituted 4,5-diphenyloxazoles. The synthesis of this system was straightforward and involved treating the appropriate sodium alkoxide with 2-chloro-4,5-diphenyloxazole. Thermolysis of a sample of 2-(allyloxy)oxazole **5** in benzene–pyridine at 155 °C for 2 h gave 3-allyl-4,5-diphenyl-4-oxazolin-2-one (**6**, 85%; Scheme I). The identity of **6** was determined by its straightforward spectral characteristics and by comparison with an independently synthesized sample prepared by treating 4,5-diphenyl-4-oxazolin-2-one (**7**) with sodium hydride and allyl bromide. All attempts to induce the extrusion of carbon dioxide from **6** failed. In contrast to the thermal results, the photolysis of oxazole **5** gave 5-allyl-4,5-diphenyl-3-oxazolin-2-one (**8**) as the only detectable photoproduct in 77% yield. Again, this system failed to extrude carbon dioxide under a variety of conditions. In order to determine whether oxazolinone **6** is an intermediate in the photochemical conversion of **5** to **8**, a sample of **6** was subjected to photolysis. The only product isolated from the irradiation was 3-allylphenanthro[9,10-*d*]oxazol-2-one (**9**). No detectable quantities of oxazolinone **8** could be found in the crude photolysate. Rigidly held stilbene moieties are known to yield phenanthrene derivatives on irradiation and provide an excellent precedent for this transformation.[12-16]

Attention was next turned to the thermolysis of the 2-propynyloxy-substituted oxazole **10**. Heating a sample of **10** afforded a single rearranged compound in 90% yield whose structure is assigned as 4,5-diphenyl-3-propadienyl-4-oxazolin-2-one (**11**).



10 **11**

In order to provide further support for the [3,3] character of the rearrangement, the thermolyses of oxazoles **12** and **13** were carried out. The exclusive formation of oxazolinones **14** and **15** is only compatible with the [3,3]-sigmatropic rearrangement route.

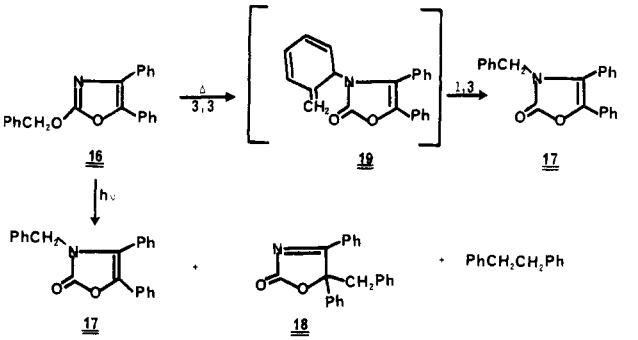


12; R=H
13; R=CH_3

14; R=H
15; R=CH_3

We have also studied the rearrangement of the closely related 2-benzyloxy-substituted oxazole **16**. In this case the thermolysis afforded 3-benzyl-4,5-diphenyloxazolinone (**17**) as the exclusive product (Scheme II). The structure of **17** was confirmed by comparison with an authentic

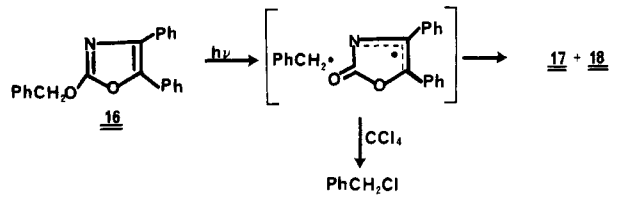
Scheme II



16 **19** **17**

17 **18**

sample. In contrast, the photolysis of **16** produced a mixture (2:3) of both the 3-benzyl- (**17**) and the 5-benzyloxazolinone (**18**) in addition to dibenzyl (24%). The formation of **17** is of some interest since it does not correspond to a simple [3,3]-sigmatropic rearrangement. One possible explanation to account for the formation of **17** involves a radical scission–recombination route. An alternate path which could also rationalize the rearrangement involves the formation of **19** via the [3,3]-sigmatropic route followed by a rapid 1,3 shift of the amido group. At the current time the available data do not distinguish between both possibilities although our inability to trap the benzyl radical (vide infra) in the thermolysis reaction is more compatible with the latter route. We believe that the photolysis of oxazole **16** involves C–O bond scission to give a radical pair which subsequently recombines to produce a mixture of oxazolinones **17** and **18**. The



16

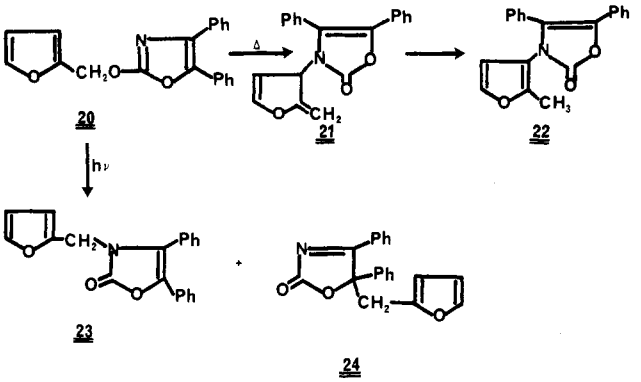
preferential formation of **18** is to be expected since the transition state associated with this reaction prefers to localize the odd electron on the phenylated carbon atom. Support for this mechanism comes from carrying out the photolysis of **16** in carbon tetrachloride. Under these conditions oxazolinone formation is almost totally suppressed. The isolation of benzyl chloride in high yield is perfectly consistent with the dissociation–reassociation path for the excited-state reaction.

We also examined the chemistry of the 2-furfuryloxy-substituted oxazole system. Heating a sample of **20** at 90 °C for 6 h gave 3-(4,5-diphenyl-2-oxooxazolyl)-2-methylfuran (**22**, Scheme III). When the thermolysis of **20** was carried out at 60 °C, the product derived from a [3,3]-sigmatropic shift (i.e., **21**) could be isolated in high yield. The initially formed oxazolinone **21** was readily converted to **22** on further heating or by stirring in benzene with a trace of *p*-toluenesulfonic acid. In contrast to the thermal results, the photolysis of **20** produced a mixture of 3- (**23**, 27%) and 5-furfuryloxazolinone (**24**, 34%), presumably by way of a radical pair intermediate.

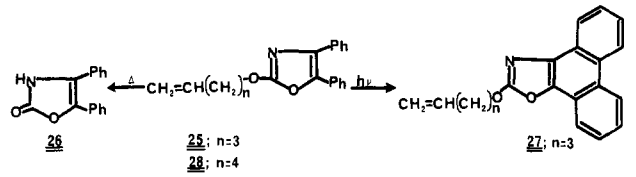
The high reactivity of oxazoles in the Diels–Alder reaction has led to their widespread use in organic synthesis.[17] Reaction with alkenes leads directly to highly substituted pyridine derivatives,[18,19] whereas cycloaddition

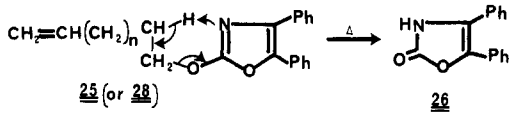
(12) Lappin, G. R.; Zanucci, J. S. *J. Org. Chem.* **1971**, *36*, 1808.
(13) Schoenberg, A.; Sidky, M. M. *Chem. Ber.* **1974**, *107*, 1207.
(14) Mudry, C. A.; Frasca, A. R. *Tetrahedron* **1974** *30*, 2983.
(15) Couture, A.; Lablache-Combier, A.; Ofenberg, H. *Tetrahedron Lett.* **1974**, 2497.
(16) Padwa, A.; Ku, H.; Mazzu, A. *J. Org. Chem.* **1978**, *43*, 381.
(17) Katritzky, A. R.; Boulton, A. J. *Adv. Heterocycl. Chem.* **1974**, *17*, 99.
(18) Firestone, R. A.; Harris, E. E.; Reuter, W. *Tetrahedron* **1967**, *23*, 943.

Scheme III

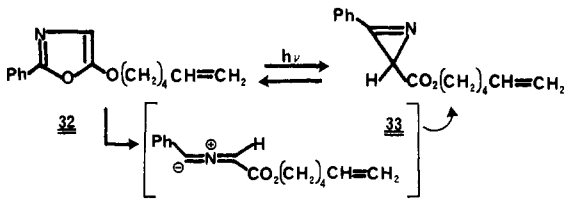


with acetylenic dipolarophiles followed by nitrile extrusion provides highly substituted furans.[20] Although the intramolecular version of the Diels–Alder reaction has received considerable attention,[21,22] little work has been devoted so far to the case where an oxazole functions as a diene partner.[23] We decided to investigate the scope of the intramolecular Diels–Alder cycloaddition of a number of oxazole derivatives related to those outlined above. Substrates in which the oxazole nucleus and the π bond are connected by an alkoxy-containing side chain (i.e., **25** and **28**) showed no evidence of ring closure. In fact, these compounds, when heated in a sealed NMR tube remained unchanged up to temperatures of 230 °C. Flash vacuum pyrolysis of either substrate (650 °C (0.002 mm)) produced 4,5-diphenyloxazol-2-one (**26**) which is the product corresponding to an intramolecular ene reaction.[25] Irradiation of **25** gave phenanthro[9,10-*b*]oxazole **27** as the sole photoproduct. One possible explanation as to why these systems do not react is that the intramolecular [4 + 2]-cycloaddition occurs only when the substrate adopts a conformation in which the oxazole and the π bond of the dienophile are geometrically disposed for π overlap. Reactivity in the cycloaddition is heavily dependent on factors which favor this conformation. Substrates such as **25** or **28**, in which the side chain contains an alkoxy group, do not cycloadd presumably since the intramolecular ene reaction represents a lower energy pathway, perhaps as a result of conformational factors. In addition, the formation of a stable carbonyl group in the final product undoubtedly facilitates this mode of reaction.

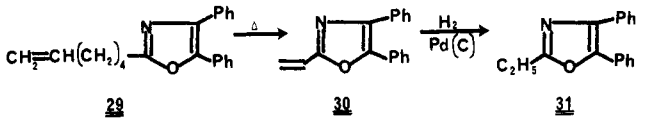




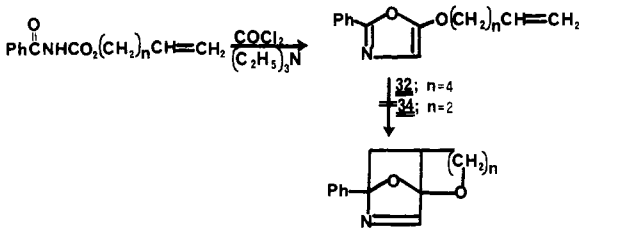
Scheme IV



At this point it seemed worthwhile to study a related system in which carbonyl group formation in the ene reaction would not occur. This would remove the driving force for the formation of the ene product. With this in mind we prepared 4,5-diphenyl-2-(5-hexenyl)oxazole (**29**) and examined its thermal behavior. Structure **29** was synthesized in good yield by treating 2-methyl-4,5-diphenyloxazole with lithium diisopropylamide and quenching the resulting carbanion with 1-bromo-4-pentene. Flash vacuum pyrolysis of **29** afforded 2-vinyl-4,5-diphenyloxazole (**30**) as the only identifiable product. Hydrogenation of **30** over palladium on carbon gave the reduced oxazole **31** whose structure was verified by comparison with an authentic sample. It is not clear how vinyloxazole **30** is formed from the thermolysis of **29**.



We also prepared and studied an oxazole which did not contain the 4,5-diphenyl substitution pattern with the hope that it would be much easier for this system to undergo intramolecular [4 + 2]cycloaddition. A study of the effect of substituents on the reactivity of oxazoles under Diels–Alder conditions has shown that 5-alkoxy-substituted oxazoles are among the most reactive systems.[17] With this in mind, we prepared oxazoles **32** and **34** by phosgene dehydration of the appropriately esterified amino acids. Surprisingly, both compounds resisted all attempts to effect the desired cycloaddition. Suspicions about an extremely facile retro-Diels–Alder reaction led us to lower the temperatures, but even at 25 °C the NMR spectra did not reveal a trace of the elusive cycloadducts. Our inability to obtain an intramolecular Diels–Alder cycloadduct from the above systems may be due to several factors. There have been reports in the literature which indicate that phenyl substituents in the 2- or 5-position of the oxazole ring inhibit [4 + 2]cycloadditions.[17] This could be due to either steric crowding in the transition state or to a deconjugative effect of the phenyl group with the π electrons of the oxazole ring. Also, with these systems, the energy gap between the HOMO and LUMO orbitals may be too large for efficient cycloaddition to occur.

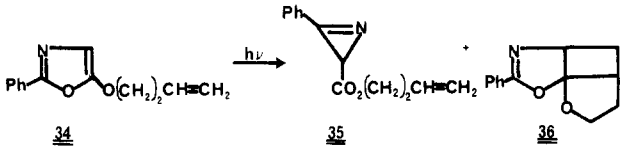


In view of the lack of thermal reactivity of **32** and **34** and the knowledge that oxazoles undergo photoisomerization to isoxazoles,[26] we decided to investigate the photochemical

(19) Kozikowski, A. P.; Hasan, N. M. *J. Org. Chem.* **1977**, *42*, 2039.
(20) Grigg, R.; Hayes, R.; Jackson, J. L. *J. Chem. Soc. D* **1969**, 1167. Grigg, R.; Jackson, J. L. *J. Chem. Soc. C* **1970**, 552.
(21) Oppolzer, W. *Angew. Chem.* **1977**, *89*, 10.
(22) Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63.
(23) Although a limited number of examples of the intramolecular Diels–Alder reaction of the oxazole nucleus have been reported,[24] no systematic study has appeared.
(24) Jacobi, P. A.; Craig, T. *J. Am. Chem. Soc.* **1978**, *100*, 7748. Jacobi, P. A.; Walker, D. G.; Odeh, I. M. A. *J. Org. Chem.* **1981**, *46*, 2065. Jacobi, P. A.; Walker, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 4611.
(25) For a recent review, see: Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476.

behavior of these two systems. Irradiation of the 5-hexenyloxy-substituted isomer **32** afforded the azirinyl ester **33** (Scheme IV) in 54% yield as the exclusive photoproduct. The photochemical formation of azirines from oxazoles is well documented in the literature and provides a good analogy for this transformation.[26-28] The reaction has been envisaged as proceeding via a reactive excited state which undergoes dissociative cleavage at the C_2–O bond to generate a transient nitrile ylide. The photochemical behavior of azirine **33** was also examined and was found to regenerate oxazole **32** when Corex-filtered light was used. The formation of **32** requires that electrocyclization of the nitrile ylide intermediate proceed at a faster rate than intramolecular cycloaddition across the olefinic π bond. The slow rate of the cycloaddition is probably related to the fact that nitrile ylides generally do not add to simple olefins since such a pair of addends possesses a large dipole HOMO–dipolarophile LUMO gap.[29] Because of their high nucleophilicities, nitrile ylides generally undergo reactions with their precursors, dimerize, or isomerize faster than they undergo reactions with alkyl-substituted alkenes.[30,31]

We also studied the photochemistry of oxazole **34**. With this system a mixture of two products was produced. In addition to the expected ring-contracted product (**35**, 41%), an intramolecular [2 + 2] cycloadduct was also



34 35 36

formed in 34% yield. Careful examination of the NMR spectrum led us to assign **36** as the structure of this material (see Experimental Section). Although [2 + 2] photocycloadditions of olefins to other olefins[32] and to ketones are well characterized,[33] only a few examples of cycloadditions across heterocyclic rings are known.[34] Taking into account the results of earlier studies on intramolecular photocycloadditions,[32] it would appear that the most likely initial step involves excitation of the heterocyclic ring followed by addition to the π bond and subsequent radical coupling. Inspection of molecular models of **34** indicates that the π bonds of the oxazole and olefinic system can easily approach each other in parallel planes, and consequently intramolecular cycloaddition can readily occur. It should also be pointed out that there was no evidence for the formation of cross-addition products from the photolysis of **34**. In this case the stability of the initially formed diradical is apparently the critical factor which controls the regiochemical outcome of the cycloaddition.

Experimental Section[35]

Preparation of 2-(Allyloxy)-4,5-diphenyloxazole (5). To a 3.22-g sample of allyl alcohol in 15 mL of tetrahydrofuran was added small quantities of sodium metal until the hydrogen evolution had ceased. The resulting mixture was added to a stirred solution containing 1.0 g of 2-chloro-4,5-diphenyloxazole in 12 mL of tetrahydrofuran. To this mixture were added 0.5 mL of hexamethylphosphoramide and 2.00 g of molecular sieves. After the mixture was stirred at room temperature for 48 h, water was added to the reaction mixture. 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 1.08 g (94%) of a yellow oil. This material was subjected to chromatography by using a basic alumina column with a 3% acetone–hexane mixture as the eluent. The major fraction contained 990 mg of a clear oil which was crystallized from a 15% ethyl acetate–hexane solution to give 2-(allyloxy)-4,5-diphenyloxazole (**5**) as a white crystalline solid: mp 56–57 °C; NMR ($CDCl_3$, 90 MHz) δ 4.80–4.97 (m, 2 H), 5.14–5.54 (m, 2 H), 5.80–6.27 (m, 1 H), 7.04–7.74 (m, 10 H); IR (KBr) 1620, 1570, 1555, 1490, 1440, 1370, 1345, 1315, 1215, 1000, 960, 830, 745, 735 cm^{-1}; UV (cyclohexene) 302 nm (ϵ 21 800); MS, *m/e* 277, 236, 210, 208, 106, 105. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.80; H, 5.50; N, 5.03.

Thermolysis of 2-(Allyloxy)-4,5-diphenyloxazole (5). A solution containing 82 mg of **5** in 3 mL of a 90:10 benzene/pyridine mixture was sealed under an argon atmosphere in a Carius tube. The tube was heated in a thermostated oil bath at 155 °C for 2 h. Removal of the solvent left a yellow oil which was subjected to silica gel column chromatography by using a 25% ethyl acetate–hexane mixture as the eluent. The major fraction isolated from the column contained 70 mg (85%) of a colorless oil which crystallized upon standing to give a white crystalline solid (mp 82–83 °C) whose structure was assigned as 3-allyl-4,5-diphenyl-4-oxazolin-2-one (**6**): NMR ($CDCl_3$, 90 MHz) δ 3.20 (dd, 1 H, J = 14.0, 6.0 Hz), 3.55 (dd, 1 H, J = 14.0, 6.0 Hz), 4.87–5.24 (m, 2 H), 5.54–5.98 (m, 1 H), 7.11–7.61 (m, 10 H); IR (KBr) 3485, 2980, 1750, 1590, 1490, 1440, 1340, 1295, 1265, 1145, 1115, 1040, 1015, 995, 915, 760, 745 cm^{-1}; UV (cyclohexane) 278 nm (ϵ 14 600); MS, *m/e* 278, 277, 236, 208, 165. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.86; H, 5.45; N, 5.04.

An authentic sample of the above compound was prepared in the following fashion. To a 1.5-g sample of a 50% sodium hydride oil dispersion in 30 mL of dry *N,N*-dimethylformamide was added 6.0 g of 4.5-diphenyl-4-oxazolin-2-one (**7**) at 0 °C under a nitrogen atmosphere. After the mixture was stirred at 0 °C for 30 min, 3.46 g of allyl bromide was slowly added to the reaction mixture. The mixture was stirred at room temperature for 2 h and was then quenched with water. The mixture was concentrated under reduced pressure, and the resulting residue was taken up in ether and washed four times with water. The ether layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure to leave 3.85 g (55%) of 3-allyl-4,5-diphenyl-4-oxazolin-2-one (**6**) which was identical with the material obtained from the thermolysis of 2-(allyloxy)-4,5-diphenyloxazole (**5**).

Photolysis of 2-(Allyloxy)-4,5-diphenyloxazole (5). A solution containing 120 mg of **5** in 175 mL of benzene was irradiated for 165 min with a 550-W Hanovia mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left a yellow oil which was subjected to flash chromatography by using a 13% acetone–hexane mixture as the eluent. The major fraction isolated from the column contained 95 mg (77%) of a yellow crystalline solid. Recrystallization of this material from a 20% acetone–hexane mixture afforded a white crystalline solid (mp 100–101 °C) whose structure was assigned

(26) For a recent review see: Padwa, A. "Rearrangement in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, p 501.

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(32) Baldwin, S. W. *Org. Photochem.* **1981**, *5*, 123.

(33) Jones, G. *Org. Photochem.* **1981**, *5*, 1.

(34) For some leading references, see: Davis, P. D.; Neckers, D. C.; Blount, J. R. *J. Org. Chem.* **1980**, *45*, 462. Kulyk, M. S.; Neckers, D. C. *J. Org. Chem.* **1982**, *47*, 4914.

(35) 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 by 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 Finnigan 4000 mass spectrometer at an ionizing voltage of 70 eV.

as 5-allyl-4,5-diphenyl-3-oxazolin-2-one (8): NMR ($CDCl_3$, 90 MHz) δ 3.20 (dd, 1 H, J = 14.0, 6.0 Hz), 3.55 (dd, 1 H, J = 14.0, 6.0 Hz), 4.93–5.26 (m, 2 H), 5.35–5.82 (m, 1 H), 7.27–7.63 (m, 8 H), 7.83–8.00 (m, 2 H); IR (KBr) 1776, 1591, 1561, 1446, 1331, 1246, 1173, 984, 946, 760 cm^{-1}; UV (cyclohexane) 266 nm (ε 17 520), 215 (19 160); MS, m/e 277 (M^+), 237, 236, 130, 129. Anal. Calcd from $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.72; H, 5.52; N, 4.99.

Photolysis of 3-Allyl-4,5-diphenyl-4-oxazolin-2-one (6). A solution containing 150 mg of **6** in 200 mL of benzene was irradiated for 12.5 h with a 450-W Hanovia lamp equipped with a Vycor filter sleeve. Removal of the solvent under reduced pressure left a crude brown oil which was subjected to flash silica gel column chromatography with a 20% ethyl acetate–hexane mixture as the eluent. The major fraction contained 105 mg (71%) of a yellow residue which was crystallized from 95% ethanol and sublimed at 130 °C (0.05 mm) to give 79 mg (53%) of a white crystalline solid (mp 185–186 °C) whose structure was assigned as 3-allylphenanthro[9,10-*d*]oxazol-2-one (**9**): NMR ($CDCl_3$, 90 MHz) δ 4.87–5.01 (m, 2 H), 5.16–5.44 (m, 2 H), 5.93–6.37 (m, 1 H), 7.50–7.84 (m, 4 H), 7.97–8.24 (m, 2 H), 8.62–8.91 (m, 2 H); IR (KBr) 1754, 1634, 1609, 1509, 1442, 14198 1339, 13258 1015, 961, 906 cm^{-1}; MS m/e 276, 275, 235, 2348 206; UV (cyclohexane) 322 nm (ε 12 900), 308 (12 222), 274 (18 300), 264 (33 900), 247 (52 500). Anal. Calcd for $C_{18}H_{15}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.23; H, 4.87; N, 4.99.

Preparation and Thermolysis of 2-(2-Propynyloxy)-4,5-diphenyloxazole (10). This material was prepared in 81% yield by using a procedure identical with that described for oxazole **5**: mp 75–76 °C; NMR ($CDCl_3$, 90 MHz) δ 2.56 (t, 1 H, J = 2.7 Hz), 8.00 (d, 2 H, J = 2.7 Hz), 7.11–7.71 (m, 10 H); IR (KBr) 3320, 3075, 2145, 1670, 1605, 1500, 1443, 1392, 1358, 1328, 1230, 1010, 975, 758; UV (cyclohexane) 298 nm (ε 12 100); MS, m/e 275, 274, 236, 208, 128. Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.54; H, 4.78; N, 5.04.

A solution containing 340 mg of **10** in 4 mL of a 80:20 benzene/pyridine mixture was sealed under an argon atmosphere in a Carius tube. The tube was heated in a thermostated oil bath at 158 °C for 75 min. Removal of the solvent under reduced pressure lefat a dark brown oil which was subjected to flash chromatography with a 94:4:2 hexane/triethylamine/acetone mixture as the eluent. The major fraction isolated from the column contained 300 mg (90%) of a solid (mp 104–105 °C) whose structure was assigned as 4,5-diphenyl-3-(propadienyl)-4-oxazolin-2-one (**11**): NMR ($CDCl_3$, 90 MHz) δ 4.98 (d, 2 H, J = 6.6 Hz), 6.45 (t, 1 H, J = 6.6 Hz), 6.80–7.92 (m, 10 H); IR (KBr) 3075, 2940, 2255, 1755, 1640, 1585, 1495, 1440, 1360, 1250, 1050, 1015, 900, 745, 715, 680 cm^{-1}; MS, m/e 275 (M^+), 274, 231, 230, 203, 178; UV (cyclohexane) 299 nm (ε 15 510), 223 (16 330). Anal. Calcd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.88; H, 4.78; N, 5.05.

Preparation of 2-(Benzyloxy)-4,5-diphenyloxazole (16). By use of a procedure similar to that used for the preparation of 2-(allyloxy)-4,5-diphenyloxazole, benzyl alcohol was allowed to react with 2-chloro-4,5-diphenyloxazole in tetrahydrofuran, and the mixture was chromatographed to give 300 mg (71%) of a white crystalline solid (mp 79–80 °C) whose structure was assigned as 2-(benzyloxy)-4,5-diphenyloxazole (**16**): NMR (CCl_4, 90 MHz) δ 5.58 (s, 2 H), 7.34–8.01 (m, 15 H); IR (neat) 1600, 1500, 1445, 1390, 1360, 1335, 1230, 1010, 755, 700, 685 cm^{-1}; MS, m/e 327 (M^+), 237, 236, 208, 105, 91; UV (cyclohexane) 302 nm (ε 14 260), 224 (24 170). Anal. Calcd for $C_{22}H_{17}NO_2$: C, 80.74; H, 5.23; N, 4.28. Found: C, 80.54; H, 5.28; N, 4.25.

Thermolysis of 2-(Benzyloxy)-4,5-diphenyloxazole (16). A solution containing 500 mg of **16** in 0.4 mL of a 4:1 benzene/pyridine mixture was sealed in an NMR tube and heated at 130 °C for 24 h. The solvent was removed under reduced pressure, and the residue was subjected to silica gel chromatography with a 20% acetone–hexane mixture as the eluent to give 200 mg (40%) of 3-benzyl-4,5-diphenyl-4-oxazolin-2-one (**17**) as a yellow crystalline solid [mp 95–96 °C (lit.[36] mp 92–93 °C)] whose spectral data were identical in every detail with those of an authentic sample: NMR ($CDCl_3$, 90 MHz) δ 4.60 (s, 2 H), 6.89–7.50 (m, 10 H); IR (KBr) 3070, 3040, 1760, 1500, 1450, 1385, 1350, 1245, 1060, 1030, 753, 705 cm^{-1}. Anal. Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.77; H, 5.25; N, 4.28.

Photolysis of 2-(Benzyloxy)-4,5-diphenyloxazole (16). A solution containing 380 mg of **16** in 250 mL of benzene was irradiated for 2 h with a 550-W Hanovia mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left behind a yellow oil which was subjected to flash silica gel chromatography with an 88:10:2 hexane/acetone/triethylamine mixture as the eluent. The first fraction contained 50 mg (24%) of dibenzyl. The second fraction isolated from the column contained 90 mg (24%) of 3-benzyl-4,5-diphenyl-4-oxazolin-2-one (**17**). The last fraction isolated consisted of 110 mg (29%) of a white crystalline solid (mp 170–171 °C) whose structure was assigned as 5-benzyl-4,5-diphenyl-3-oxazolin-2-one (**18**): NMR ($CDCl_3$, 90 MHz) δ 3.73 (d, 1 H, J = 12.9 Hz), 3.80 (d, 1 H, J = 12.9 Hz), 6.75–7.85 (m, 15 H); IR (KBr) 1788, 1595, 1560, 1450, 1370, 1230, 1150, 975, 945, 775, 768, 760, and 690 cm^{-1}; UV (cyclohexane) 265 nm (ε 15 820), 215 (25 640); MS, m/e 237, 236, 180, 179, 178, 165. Anal. Calcd for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.24; N, 4.28. Found: C, 80.73; H, 5.25; N, 4.26.

Preparation of 2-[(2-Butenyl)oxy]-4,5-diphenyloxazole (12). By use of a procedure similar to that used for the other alkyloxy-substituted oxazoles, crotyl alcohol was allowed to react with 2-chloro-4,5-diphenyloxazole in tetrahydrofuran. Chromatography of the mixture afforded 2-[(2-butenyl)oxy]-4,5-diphenyloxazole (**12**): 80%; mp 60–61 °C; NMR ($CDCl_3$, 90 MHz) δ 1.69 (d, 3 H, J = 6.0 Hz), 4.81–4.97 (d, 2 H, J = 6.0 Hz), 5.73–5.93 (m, 2 H), 7.13–7.77 (m, 10 H); IR (KBr) 3060, 2975, 1598, 1445, 1328, 1325, 1227, 1007, 965, 940, 900, 650 cm^{-1}; UV (cyclohexane) 302 nm (ε 13 760), 224 (21 300); MS, m/e 305, 236, 123, 121, 119. Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.29; H, 5.88; N, 4.79.

Thermolysis of 2-[(2-Butenyl)oxy]-4,5-diphenyloxazole (12). A solution containing 660 mg of **12** in 5 mL of a 80:20 benzene/pyridine mixture was sealed under an argon atmosphere in a Carius tube. The tube was heated in a thermostated oil bath at 158 °C for 2 h. Removal of the solvent under reduced pressure left a yellow oil which was subjected to silica gel column chromtography with a 25% ethyl acetate/hexane mixture as the eluent. The major fraction isolated from the column contained 640 mg (97%) of a white crystalline solid (mp 99–100 °C) whose structure was assigned as 3-(1-methylallyl)-4,5-diphenyl-4-oxazolin-2-one (**14**): NMR ($CDCl_3$, 90 MHz) δ 1.82 (d, 3 H, J = 7.2 Hz), 3.67–4.37 (m, 1 H), 4.98 (dd, 1 H, J = 11.4, 1.0 Hz), 5.13 (dd, 1 H, J = 5.4, 1.0 Hz), 5.88–6.30 (m, 1 H), 7.00–7.63 (m, 10 H); IR (KBr) 3080, 3005, 2955, 1760, 1580, 1495, 1445, 1360, 1330, 1255, 1050, 1015, 915, 750, 730, 690 cm^{-1}; MS, m/e 291, 238, 237, 236, 208; UV (cyclohexane) 302 nm (ε 14 040), 292 (13 520), 217 (15 700). Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.13; H, 5.90; N, 4.77.

Preparation of 2-[(3-Methyl-2-butenyl)oxy]-4,5-diphenyloxazole (13). By use of a procedure similar to that employed with the other alkyloxy-substituted oxazoles, 3-methyl-2-butenol was treated with 2-chloro-4,5-diphenyloxazole in tetrahydrofuran. Chromatography of the crude reaction mixture gave a 49% yield of 2-[(3-methyl-2-butenyl)oxy]-4,5-diphenyloxazole (**13**) as a pale yellow oil: NMR (CCl_4, 90 MHz) δ 1.81 (s, 6 H), 4.93 (d, 2 H, J = 7.5 Hz), 5.56 (br, t, 1 H, J = 7.5 Hz), 7.16–7.73 (m, 10 H); IR (neat) 3075, 1600, 1525, 1447, 1360, 1318, 1235, 1200, 1125, 1050, 1017, 968, 760, 670 cm^{-1}; MS, m/e 123, 121, 119, 117, 86, 84, 82; UV (cyclohexane) 284 nm (ε 14 090), 215 (30 000).

The minor component isolated from the column contained 340 mg (30%) of a white drystalline solid (mp 115–116 °C) whose structure was assigned as 3-(1,1-dimethylallyl)-4,5-diphenyl-4-oxazolin-2-one (**15**): NMR (CCl_4, 90 MHz) δ 1.51 (s, 6 H), 4.64 (d, 1 H, J = 10.5 Hz), 4.77 (d, 1 H, J = 15 Hz), 5.84 (dd, 1 H, J = 15, 10.5 Hz); IR (KBr) 3075, 2990, 2945, 1745, 1640, 1595, 1439, 1355, 1290, 1260, 1128, 995, 910, and 740 cm^{-1}; UV (cyclohexane) 297 nm (ε 14 240), 287 (16 900), 213 (15 930); MS, m/e 305 (M^+), 238, 237, 165, 105. Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.67; H, 6.27; N, 4.59. Found: C, 78.55; H, 6.28; N, 4.58.

As a result of the lability of 2-[(3-methyl-2-butenyl)oxy]-4,5-diphenyloxazole (**13**), this compound could not be fully characterized. A solution containing this substrate readily rearranged

(36) Hakimelahi, G. H.; Boyce, C. B.; Kasmai, H. S. *Helv. Chim. Acta* **1977**, *60*, 342.

at room termperature to 3-(1,1-dimethylallyl)-4,5-diphenyl-4-oxazolin-2-one (**15**).

Preparation of 2-(Furfuryloxy)-4,5-diphenyloxazole (20). By use of a procedure similar to that employed with related alkyoxy-substituted oxazoles, a sample of furfuryl alcohol was allowed to react with 2-chloro-4,5-diphenyloxazole in tetrahydrofuran. Silica gel chromatography of the reaction mixture gave 300 mg (31%) of a pale yellow oil whose structure was assigned as 2-[(furfuryl)oxy]-4,5-diphenyloxazole (**20**): NMR (CCl_4, 90 MHz) δ 5.39 (s, 2 H), 6.29 (dd, 1 H, J = 2 Hz), 6.52 (dd, 1 H, J = 3.5 Hz), 7.10–7.63 (m, 11 H); IR (neat) 3101, 3071, 3001, 2951, 1596, 1526, 1443, 1356, 1211, 1196, 1046, 966, 896, 756 cm^{-1}; UV (cyclohexane) 298 nm (ϵ 14 030), 224 (32 950). Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.68; H, 4.82; N, 4.31.

Thermolysis of 4,5-Diphenyl-2-(furfuryloxy)oxazole (20). A solution containing 430 mg of **20** in 6 mL of an 80:20 mixture of benzene/pyridine was sealed under an argon atmosphere in a Carius tube. The tube was heated at 60 °C in an oil bath for 10 h. After the mixture cooled to room termperature, the solvent was removed under reduced pressure, and the resulting residue was triturated with a 30% ethyl acetate–hexane mixture to give 311 mg (72%) of a crystalline solid. Recrystallization of this material from a 60% ethyl acetate–hexane mixture gave 3-(4,5-diphenyl-oxooxazolyl)-2-ethenyl-3*H*-furan (**21**) as a white crystalline solid: mp 161–162 °C; NMR ($CDCl_3$, 90 MHz) δ 4.11 (d, 1 H, J = 2.4 Hz), 4.45 (d, 1 H, J = 2.4 Hz), 5.75 (dd, 1 H, J = 6.0 Hz, 1.5 Hz), 6.20 (t, 1 H, J = 1.5 Hz), 6.33 (dd, 1 H, J = 6.0, 1.5 Hz), 7.27–7.76 (m, 8 H), 7.84–8.00 (m, 2 H); IR (KBr) 1784, 1647, 1588, 1561, 1441, 1318, 1288, 1213, 1163, 1038, 948, 765 cm^{-1}; MS m/e 317, 2378, 236, 186, 170; UV (cyclohexane) 271 nm (ϵ 10 110), 267 (10 380), 217 (11mtc600). Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.57; H, 4.82; N, 4.36.

Treatment of **21** in 0.4 mL of deuteriochloroform with a trace of *p*-toluenesulfonic acid resulted in an instantaneous rearrangement to 3-(4,5-diphenyl-2-oxooxazolyl)-2-methylfuran (**22**): NMR (CCl_4, 90 MHz) δ 2.21 (s, 3 H), 4.97 (t, 1 H, J = 3.0 Hz), 6.23 (t, 1 H, J = 3.0 Hz), 7.25–7.78 (m, 8 H), 7.82–8.05 (m, 2 H); IR (KBr) 3099, 2954, 1779, 1596, 1561, 1443, 1319, 1291, 1159, 1009, 977, 941, 766 cm^{-1}; UV (cyclohexane) 295 nm (ϵ 13 100), and 218 (25 040); MS, m/e 317, 235, 186, 170, 155. Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.67; H, 4.89; N, 4.35.

Photolysis of 4,5-Diphenyl-2-(furfuryloxy)oxazole (20). A solution containing 400 mg of **20** in 250 mL of benzene was irradiated for 2 h by using a 550-W Hanovia Mercury arc lamp equipped with a Pyrex filter sleeve. Removal of the solvent under reduced pressure left behind a yellow oil which was subjected to flash silica gel chromatography with a 76:14:10 hexane/acetone/triethylamine mixture as the eluent. The first fraction isolated from the column contained 109 mg (27%) of a yellow oil whose structure was assigned as 4,5-diphenyl-3-furfuryl-4-oxazolin-2-one (**23**): NMR (CCl_4, 90 MHz) δ 4.51 (s, 2 H), 5.92 (d, 1 H, J = 3.0 Hz), 6.12 (t, 1 H, J = 3.0, 1.0 Hz), 6.77–7.58 (m, 11 H); IR (neat) 3057, 1757, 1659, 1595, 1494, 1439, 1337, 1242, 1202, 1137, 1045, 900 cm^{-1}; UV (cyclohexane) 299 nm (ϵ 13 290), and 216 (25,110); MS m/e 317, 237, 236, 186, 170. Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.68; H, 4.92; N, 4.26.

The structure of this material was further verified by an independent synthesis. To a solution containing 4.0 g of furfuryl alcohol in 50 mL of absolute ether was added, at 0 °C, 4.0 g of phosphorous tribromide over a period of 20 min. The reaction mixture was allowed to warm to room temperature and was stirred at this temperature for 30 min. The dark solution was decanted into a clean flask and was treated cautiously at 0 °C with 10 mL of a 40% sodium hydroxide solution. The ether layer was separated from the aqueous layer and was kept over solid sodium hydroxide in the refrigerator. To a 170-mg sample of 50% sodium hydride oil dispersion in 10 mL of dry *N,N*-dimethylformamide was added 500 mg of 4,5-diphenyl-4-oxazolin-2-one at 0 °C under a nitrogen atmosphere. After the mixture was stirred for 30 minutes, a solution containing 4 mL of a 0.80 M solution of furfuryl bromide in ether was slowly added to the reaction mixture at 0 °C. The mixture was stirred at room temperature for 4 h, and water was then added. The organic layer was separated, and the solvent was removed under reduced pressure to give a yellow residue which was taken up in ether. The ether layer was washed four times with water, dried over magnesium sulfate, and then removed under reduced pressure to leave behind a yellow residue. Subjection of the residue to silica gel column chromatography with a 25% acetone/hexane mixture as the eluent gave 596 mg (89%) of **23** which was identical with the material obtained from the photolysis of **20**.

The second fraction isolated from the crude photolysate derived from the irradiation of **20** contained 108 mg (34%) of a yellow crystalline solid which was recrystallized from carbon tetrachloride to give a light yellow solid which was identified as 4,5-diphenyl-5-furfuryl-3-oxazolin-2-one (**24**): NMR ($CDCl_3$, 90 MHz) δ 3.85 (dd, 1 H, J = 18.0, 15.0 Hz), 4.08 (dd, 1 H, J = 18.0, 15.0 Hz), 6.01 (d, 1 H, J = 3.0 Hz), 8.2 (dd, 1 H, J = 4.5, 3.0 Hz), 7.12–7.94 (m, 11 H); IR (KBr) 3069, 1784, 1593, 1561, 1494, 1447, 1339, 1266, 1201, 1151, 975 cm^{-1}; MS m/e 317, 236, 208, 165, 141; UV (cyclohexane) 265 nm (ϵ 13 000), 212 (23 150). Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41. Found: C, 75.87; H, 4.82; N, 4.40.

Thermolysis and Photolysis of 4,5-Diphenyl-2-[(4-pentenyl)oxy]oxazole (25). By use of a procedure similar to that used for the preparation of the other alkyloxy-substituted oxazoles, 4,5-diphenyl-2-[(4-pentenyl)oxy]oxazole (**25**) was prepared as a colorless oil: 80% yield; NMR ($CDCl_3$, 90 MHz) δ 1.68–2.36 (m, 4 H), 4.47 (t, 2 H, J = 6.0 Hz), 4.89–5.23 (m, 2 H), 5.60–6.07 (m, 1 H), 7.13–7.80 (m, 10 H); IR (neat) 3078, 2920, 1600, 1440, 1347, 1325, 1227, 1230, 1007, 900 cm^{-1}; UV (cyclohexane) 301 nm (ϵ 13 600), 224 (21 430); MS m/e 319, 238, 237, 236, 166, 165. Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.59; H, 6.25; N, 4.31.

A sample containing 133 mg of **25** was distilled at 135 °C (0.002 mm) through a 20 × 0.8 cm quartz tube externally heated at 650 °C. The white solid which condensed on the liquid nitrogen cold finger was removed by using ether. The ether solution was dried over magnesium sulfate and concentrated under reduced pressure to give 84 mg (90%) of a white solid (mp 205–206 °C) whose structure was identified as 4,5-diphenyloxazol-2-one (**26**) by comparison with an independently synthesized sample (lit.[37] mp 205–206 °C): NMR ($CDCl_3$, 90 MHz) δ 7.23–7.64 (m, 11 H); IR (KBr) 3475, 3215, 3070, 2870, 2795, 1755, 1600, 1495, 1445, 1385, 1300, 1265, 1115, 1050, 970, 940, 760, 740 cm^{-1}.

A solution containing 150 mg of **25** in 200 mL of benzene was irradiated for 6.5 h by using a 450-W Hanovia lamp equipped with a Corex filter sleeve. Removal of the solvent under reduced pressure left 140 mg (94%) of an orange oil. Subjection of this oil to silica gel column chromatography with a 3% acetone/hexane mixture as the eluent gave a white crystalline solid (mp 66–67 °C) whose spectral data were consistent with 2-[(4-pentenyl)-oxy]phenanthro[9,10-*b*]oxazole (**27**): NMR (CCl_4, 90 MHz) δ 1.81–2.45 (m, 4 H), 4.57–4.75 (t, 2 H, J = 6.0 Hz), 4.96–5.28 (m, 2 H), 5.64 (m, 1 H), 7.41–7.77 (m, 4 H), 7.95–8.18 (m, 1 H), 8.31–8.47 (m, 1 H), 8.60–8.78 (m, 2 H); IR (KBr) 3110, 2985, 1700, 1630, 1600, 1440, 1320, 1305, 1260, 995, 895, 735, 705 cm^{-1}; MS, m/e 303, 232, 211, 210, 203; UV (cyclohexane) 309 nm (ϵ 14 900), 297 (12 000), 264 (46 200), 253 (15 400), 237 (42 300). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.18; H, 5.65; N, 4.62. Found: C, 79.06; H, 5.48; N, 4.53.

Preparation and Thermolysis of 4,5-Diphenyl-2-[(5-hexenyl)oxy]oxazole (28). By use of a procedure similar to that used for the preparation of the other alkloxy-substituted oxazoles, 4,5-diphenyl-2-[(5-hexenyl)oxy]oxazole (**28**) was obtained as a colorless oil: 80% yield; NMR (CCl_4, 90 MHz) δ 1.42–2.29 (m, 4 H), 4.40– 4.63 (t, 2 H, J = 6.6 Hz), 4.92–5.20) (m, 2 H), 5.61–6.10 (m, 1 H), 7.18–7.83 (m, 10 H); IR (neat) 3101, 2979, 1602, 1499, 1455, 1359, 1326, 1229, 1007, 904, 654 cm^{-1}; UV (cyclohexane) 301 nm (ϵ 13 440), 224 (20 930); MS, m/e 319, 238, 237, 236, 166, 165. Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 79.08; H, 6.54; N, 4.41.

A sample containing 82 mg of **28** was distilled at 130 °C (0.002 mm) through a (20 × 0.8 cm) quartz tube which was externally heated at 700 °C. The white solid which condensed on the liquid nitrogen cold finger was removed by using ether. The ether

(37) Gomper, R.; Effenberger, F. *Chem. Ber.* **1959**, *92*, 1928.

solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give 55 mg (95%) of 4,5-diphenyloxazol-2-one (**26**).

Preparation and Thermolysis of 4,5-Diphenyl-2-(5-hexenyl)oxazole (29). To a solution containing 2.4 mL of diisopropylamine in 20 mL of tetrahydrofuran was added 12.6 mL of a 1.21 M *n*-butyllithium solution at 0 °C under a nitrogen atmosphere. The reaction mixture was allowed to stir at 0 °C for 30 min, and then 3.0 g of a solution containing 4,5-diphenyl-2-methyloxazole[38] in 20 mL of tetrahydrofuran was added. After the mixture was stirred at 0 °C for 30 min, 3.80 g of 1-bromo-4-pentene in 20 mL of tetrahydrofuran was added to the ice-cooled solution. After the reaction was quenched 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 3.02 g (78%) of a brown residue. Subjection of the residue to silica gel flash chromatography with a 4% ethyl acetate–hexane mixture as the eluent gave 1.69 g (44%) of a yellow oil whose structure was assigned as 4,5-diphenyl-2-(5-hexenyl)oxazole (**29**): NMR (CCl_4, 90 MHz) δ 1.35–2.31 (m, 6 H), 2.78 (br t, 2 H, J = 8.4 Hz), 4.84–5.15 (m, 2 H), 5.35–6.05 (m, 1 H), 7.15–7.85 (m, 10 H); IR (neat) 3090, 2955, 2880, 1640, 1605, 1570, 1498, 1445, 1215, 1055, 1020, 958, 908, 755, 685 cm^{-1}; UV (cyclohexane) 292 nm (ϵ 9980), 224 (16 270); MS, m/e 303, 302, 248, 230, 198. Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 82.97; H, 6.69; N, 4.48.

A sample containing 490 mg of **29** was distilled at 100 °C (1×10^{-3} mm) through a quart tube (20 × 0.8 cm) externally heated at 750 °C. The dark red material which condensed on the liquid nitrogen cold finger was removed by using ether as the solvent. The ether solution was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. The resulting dark red residue was subjected to flash silica gel chromatography with a 20% acetone–hexane mixture as the eluent. The major fraction isolated from the column contained 165 mg (42%) of a yellow oil whose structure was assigned as 4,5-diphenyl-2-vinyloxazole (**30**): NMR (CCl_4, 90 MHz) δ 5.25 (dd, 1 H, J = 11.0, 2.0 Hz), 6.13 (dd, 1 H, J = 18.0, 2.0 Hz), 6.66 (dd, 1 H, J = 18.0, 11.0 Hz); IR (neat) 3089, 2959, 1606, 1527, 1494, 1459, 1309, 1194, 1054, 1011, 914, 746 cm^{-1}.

Hydrogenation of a sample of **30** with palladium on carbon in ethyl acetate at 25 °C and 1 atm gave 4,5-diphenyl-2-ethyloxazole (**31**) as the only product which was identical in every detail with an independently synthesized sample: NMR (CL_4, 90 MHz) δ 1.32 (t, 3 H, J = 8.1 Hz), 2.71 (q, 2 H, J = 8.1 Hz), 7.08–7.40 (m, 6 H), 7.46–7.89 (m, 4 H); IR (neat) 3089, 3009, 2964, 1601, 1569, 1490, 1440, 1204, 1049, 950, 749 cm^{-1}; MS, m/e 249, 220, 206, 165, 117.

Preparation of 5-[(5-Hexenyl)oxy]-2-phenyloxazole (32). A mixture containing 3.5 g of hippuric acid and 2.9 g of 5-hexen-1-ol in 25 mL of chloroform was saturated with a stream of dry hydrogen chloride gas at room temperature. The resulting solution was heated under reflux overnight, cooled to room termperature and then concentrated under reduced pressure to give a yellow oil. The yellow oil was taken up in water and neutralized with a 10% sodium hydroxide solution. The solution was then extracted with ether, and the ether extracts were washed with water, a saturated sodium chloride solution, and then dried over magnesium sulfate. Removal of the solvent under reduced pressure gave a yellow oil which was distilled at 80 °C (1.0 mm) to afford 4.8 g (93%) of a colorless oil whose structure was identified as 5-hexenyl hippurate: NMR (CCl_4, 90 MHz) δ 1.22–1.66 (m, 6 H), 1.96 (br q, 2 H, J 6.9 Hz), 4.00 (br t, 4 H, J = 6.0 Hz), 4.81–5.09 (m, 2 H), 5.47 –5.97 (m, 1 H), 7.16–7.46 (m, 3 H), 7.66–7.99 (m, 2 H), 8.06–8.39 (br t, 1 H, J = 5.4 Hz); IR (neat) 3070, 2953, 1608, 1558, 1468, 1308, 1278, 1018, 908, 768 cm^{-1}; MS, m/e 242, 180, 160, 135, 134; UV (cyclohexane) 224 nm (ϵ 10 900).

To a stirred solution of 4.8 g of 5-hexenyl hippurate and 7.9 g of pyridine in 100 mL of chloroform was slowly added 8.82 mL of a 3 M phosgene solution in toluene. The mixture was stirred for 30 min at 20 °C, and for 2 h at 50 °C and was then washed with a 10% aqueous hydrogen chloride solution. After the mixture was dried over magnesium sulfate, the solvent was removed under reduced pressure to give 1.7 g (39%) of a dark brown residue. Subjection of the residue to silica gel column chromatography with a 4% acetone/hexane mixture as the eluent afforded 918 mg (21%) of a yellow oil whose structure was assigned as 5-[(5-hexenyl)oxy]-2-phenyloxazole (**32**): NMR (CCl_4, 90 MHz) δ 1.40–1.90 (m, 4 H), 2.10 (br q, 2 H, J = 6.0 Hz), 4.06 (t, 2 H, J = 6.0 Hz), 5.79 (ddt, 1 H, J = 18.0, 12.0, 6.0 Hz), 7.25–7.53 (m, 3 H), 7.77–8.04 (m, 2 H); IR (neat) 3070, 2953, 1608, 1558, 1468, 1308, 1278, 1018, 908, 768 cm^{-1}; UV (cyclohexane) 310 nm (ϵ 6770), 296 (13 100), 288 (13 260), 283 (13 260); MS, m/e 243, 172, 143, 128. Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.02; H, 6.98; N, 5.81.

Photolysis of 5-[(5-Hexenyl)oxy]-2-phenyloxazole (32). A solution containing 165 mg of **32** in 175 mL of benzene was irradiated for 7 h by using a 550-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent under reduced pressure left an orange oil which was subjected to flash silica gel column chromatography with a 20% ethyl acetate/hexane mixture as the eluent. The major fraction isolated from the column contained 90 mg (54%) of a light yellow oil whose structure was identified as 2-[(5-hexenyl)carboxy]-3-phenyl-2*H*-azirine (**33**): NMR (CCl_4, 90 MHz) δ 1.10–1.72 (m, 4 H), 2.00 (br q, 2 H, J = 7.2 Hz), 2.66 (s, 1 H), 4.07 (t, 2 H, J = 6.3 Hz), 4.76–5.13 (m, 2 H), 5.45–5.97 (m, 1 H), 7.17–7.93 (m, 5 H); IR (neat) 3081, 2951, 2876, 1771, 1720, 1604, 1448, 1331, 1262, 1186, 908, 756 cm^{-1}; MS, m/e 243, 160, 116, 106; UV (cyclohexane) 240 nm (ϵ 9500). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.86; H, 7.13; N, 5.82.

Irradiation of a sample of azirine **33** in benzene for 15 min by use of a Corex filter sleeve resulted in the formation of oxazole **32** as the only detectable photoproduct.

Preparation of 4-[(3-Butenyl)oxy]-2-phenyloxazole (34). A stream of dry hydrogen chloride gas was passed through a 7.0-g sample of hippuric acid and 5.6 g of 3-buten-1-ol in 30 mL of chloroform at room temperature. The mixture was heated under reflux overnight, and the excess hydrogen chloride gas was removed with a stream of nitrogen. The solution was concentrated under reduced pressure and the residue was taken up in water, and neutralized with a 10% sodium hydroxide solution. The solution was then extracted with ether and the ether extracts were combined and dried over magnesium sulfate. Removal of the solvent under reduced pressure left a yellow solid which was recrystallized from a 50% ethyl acetate–hexane mixture to give 6.8 g (74%) of a white crystalline solid (mp 76–77 °C) whose structure was assigned as 3-butenylhippurate: NMR ($CDCl_3$, 90 MHz) δ 2.37 (br q, 2 H, J = 6.9 Hz), 4.2 (t, 2 H, J = 3.0 Hz), 4.26 (t, 2 H, J = 6.9 Hz), 4.96–5.27 (m, 2 H), 6.57–7.05 (m, 1 H), 6.73 (br s, 1 H), 7.32–760 (m, 4 H), 7.70–7.92 (m, 2 H); IR (KBr) 3463, 2998, 2958, 1728, 1658, 1585, 1521, 1478, 1400, 1348 1288, 1205, 985, 911 cm^{-1}; UV (cyclohexane) 224 nm (ϵ 9300); MS, m/e 233, 180, 162, 161, 135, 134.

To a stirred solution of 5.1 g of 3-butenyl hippurate and 10.0 g of pyridine in 100 mL of chloroform was slowly added 10.8 mL of a 3 M phosgene solution in toluene. The mixture was stirred for 30 min at 25 °C, for a further 2 h at 50 °C, and finally washed with a 10% aqueous hydrogen chloride solution. After the mixture was dried over magnesium sulfate, the solvent was removed under reduced pressure to give 2.06 g (43%) of a dark brown residue. Subjection of the residue to silica gel column chromatography with a 20% ethyl acetate-hexane mixture as the eluent afforded 1.03 g (22%) of a yellow oil whose structure was assigned as 5-[(3-butenyl)oxy]-2-phenyloxazole (**34**): NMR (CCl_4, 90 MHz), δ 2.47 (br q, 2 H, J = 7.2 Hz), 4.05 (t, 2 H, J = 7.2 Hz), 5.01–5.30 (m, 2 H), 5.57–6.07 (m, 1 H), 6.1 (s, 1 H), 7.27–7.54 (m, 3 H), 7.81–8.11 (m, 2 H); IR (neat) 3096, 2996, 1741, 1604, 1276, 11018 1014, 911, 756, 678 cm^{-1}; MS, m/e 215, 161, 133, 116 UV (cyclohexane) 307 nm (ϵ 6700), 290 (12 850), 284 (13 200), 275 (13 100). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.37; H, 6.16; N, 6.46.

Photolysis of 5-[(3-Butenyl)oxy]-2-phenyloxazole (34). A solution containing 500 mg of **34** in 250 mL of benzene was irradiated for 35 h using a 550-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent under reduced pressure left a dark yellow oil which was subjected to flash silica gel column chromatography using a 20% ethyl acetate-hexane mixture as the

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eluent. The first fraction collected off the column contained 204 mg (41%) of a light yellow oil whose structure was identified as 2-[(5-butenyl)carboxy]-3-phenyl-2*H*-azirine (**35**): NMR (CCl_4, 90 MHz) δ 2.03 (dd, 2 H, J = 6.6, 1.0 Hz), 2.37 (s, 1 H), 3.83 (t, 2 H, J = 6.6 Hz), 4.61–4.89 (m, 2 H), 5.21–5.36 (m, 1 H), 7.16–7.36 (m, 3 H), 7.50–8.66 (m, 2 H); IR (neat) 3080, 2980, 1820, 1765, 1727, 1625, 1445, 1330, 1238, 1185, 1012, 755 cm^{-1}; MS, m/e 215, 174, 165, 161, 116; UV (cyclohexane) 238 nm (ϵ 9000). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.29; H, 5.98; N, 6.41.

The second fraction isolated contained a colorless oil that crystallized in a 25% ethyl acetate/hexane mixture to afford 167 mg (34%) of a white crystalline solid (mp 74–75 °C) whose structure was identified as 3-aza-1,6-dioxa-2-phenyltricyclo-[3.5.0^{5,9}]dec-2-ene (**36**): NMR (C_6D_6, 90 MHz) δ 1.10 (dtd, 1 H, J = 13.2, 6.5, 4.2 Hz), 1.50 (ddd, 1 H, J = 13.2, 6.5, 5.4 Hz), 1.75 (ddd, 1 H, J = 13.2, 6.5, 2.7 Hz), 1.92 (ddd, 1 H, J = 13.2, 9.0, 3.0 Hz), 2.75 (dddd, 1 H, J = 9.0, 7.8, 5.4, 4.2 Hz), 3.67 (dt, 1 H, J = 9.0, 6.5 Hz), 3.87 (dt, 1 H, J = 9.0, 6.5 Hz), 4.36 (ddd, 1 H, J = 6.5, 3.0, 1.2 Hz), 7.01–7.29 (m, 3 H), 8.16–8.40 (m, 2 H); IR (KBr) 3008, 2963, 2908, 1623, 1568, 1475, 1439, 1323, 1241, 1188, 1108, 1023, 974, 833 cm^{-1}; MS, m/e 178, 163, 144, 123, 119, 117; UV (cyclohexane) 242 nm (ϵ 11300). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.42; H, 6.08; N, 6.50.

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Phosphazenes. 4. Synthesis and Spectral Characteristics of a Series of 1-Aryl-1-alkyltetrachlorocyclotriphosphazenes[1]

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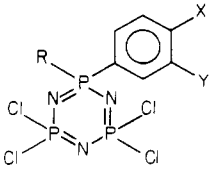
A new series of 1-aryl-1-alkyltetrachlorocyclotriphosphazenes has been synthesized. These compounds, which contain various substituents in the meta and para positions of the aryl group, have been characterized by infrared and NMR (^1H, ^{13}C, ^{19}F, and ^{31}P) spectroscopy and mass spectrometry. The ^1H and ^{13}C NMR spectra can be used to obtain a value for the Hammett σ_{para} parameter of 0.63 for the $N_3P_3Cl_4CH_3$ group, while ^{19}F NMR can be used to obtain Taft reactivity parameters of σ_I = 0.48 and σ_R = 0.16. These values are very similar to those found for a cyano group, and the similarity of the electron-withdrawing power between the $N_3P_3Cl_4CH_3$ and cyano groups is confirmed by a study of the ultraviolet spectra of the new aryl compounds.

Introduction

Over the past several years, the nature of the electronic interactions between a phosphazene ring and various exocyclic substituents has been the subject of much controversy.[2-10] Aryl-substituted phosphazenes have been subjected to examination by a wide variety of techniques, such as ultraviolet–visible spectroscopy,[3] nuclear magnetic resonance spectroscopy utilizing nuclei such as ^1H,[4] ^{13}C,[5] ^{19}F,[6] and ^{31}P,[7] electron-spin resonance spectroscopy,[8] nuclear quadrupole resonance spectroscopy observing ^{35}Cl nuclei,[9] and, finally, photoelectron spectroscopy.[10] The results of these various studies have been interpreted as indicating no,[10] little,[3,5,7] or extensive[2,4,6] resonance interactions between the aryl substituent and the phosphazene ring.

However, all of these studies to date have been limited to simple aryl- or fluoroaryl-substituted phosphazenes. This is due, in no small part, to the problems involved in the synthesis of spectroscopically instructive aryl-substituted phosphazene compounds.

In this paper we describe the synthesis and spectral characteristics of a new series of para- and meta-substituted arylchlorophosphazenes of general structure I. This



I

R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X = Y = H
R = CH_3; Y = H, X = $N(C_2H_5)_2$, $N(CH_3)_2$, OCH_3, t-C_4H_9, CH_3, C_6H_5, F, Cl, CF_3
R = CH_3; X = H; Y = $N(CH_3)_2$, OCH_3, F

is the first time that such a wide variety of aryl-substituted phosphazene compounds has been synthesized. These

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