Table VI. Observed Integrals for Determination of the Rate of Deuterium Scrambling

time, min	area H–C(5)	area H–C(2)	% D at H(2)
0	47.4	6.4	86.4
400	58.2	10.6	81.8
600	45.7	9.7	78.7
800	36.6	8.6	76.5
1000	91.0	24.4	73.2
1200	79.5	22.7	71.4

2930, 2800, 1460, 1270, 1110; mass spectrum m/z (rel intensity) 164 (m^+, 5), 132 (11), 119 (100), 91 (16).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.14; H, 9.96.

(+)-2-Deuterio-3,7-dimethyl-7-methoxymethylcycloheptatriene (8) was prepared exactly as described above for the undeuterated triene. Reduction of the resolved 2,6-dimethyl-1-ketocyclohepta-2,4-diene-6-methylene hydrogen phthalate with sodium borodeuteride gave 1-deuterio-1-hydroxy-2,6-dimethylcyclohepta-2,4-diene-6-methylene hydrogen phthalate (**5**) in quantitative yield. Acid-catalyzed dehydration of 3.6 g of alcohol **5** afforded the 2-deuterio triene **6** in 71% yield. Saponification of the hemiphthalate and methylation of the hydroxymethyl intermediate **7** gave **8**. According to NMR analysis, this triene contained 86.4% deuterium at C(2) (Figure 1); it had $[\alpha]_{365}$ +65.0, $[\alpha]_{436}$ +31.9° ($CHCl_3$), and NMR in the presence of Eu(hfbc)$_3$ employing benzene-d_6 as the solvent showed this material to be 90.7 ± 0.9% optically pure.

Sealed-Tube Kinetics. Pyrolysis tubes were constructed from 7-mm borosilicate tubing; they were soaked in a concentrated ammonium hydroxide–EDTA solution at 40 °C for 16 h, rinsed well with distilled water, and dried at 130 °C for 24 h.

The substrate was purified by VPC on the FFAP column. In a typical kinetic run, 41 mg of purified **8** was diluted to 0.5 mL with freshly distilled toluene containing 0.5% triethylamine, and the resulting solution was placed in a pyrolysis tube. The tube was placed on a high-vacuum line and degassed by two freeze–pump–thaw cycles; it was sealed under high vacuum (10^{-5} mm) to give a tube approximately 10 cm in length.

A tube was placed in a wire cage and immersed in a eutectic salt bath heated to 223.4 °C. On immersion of the tube, the temperature of the bath decreased to 223.2 °C and required 2 min to recover. The salt bath consisted of a well-insulated stainless steel beaker approximately 20-cm in diameter and 20-cm in height filled with an equimolar mixture of $NaNO_2$ and KNO_3.[35] The bath was fitted with two stainless steel immersion heaters powered through variacs and a third heater powered by a Bailey Instrument Co. Model 253 precision temperature controller. The molten salt was stirred with a "Lightnin" stirrer and the temperature was measured with a frequently calibrated Hewlett-Packard 2802 A platinum resistance thermometer.

The tube was heated for the appropriate time, removed, cooled with tap water, and opened. The contents of the tube were purified on a 6.4 mm × 2.5 m 10% DBTCP on 60/80 Chromosorb W NAW column coupled with a 6.4 mm × 0.3 m 10% SE 30 on 60/80 Chromosorb W NAW column at 120 °C with a helium flow rate of 60 mL/min. The substrate **8** and degenerate isomers **14** showed a retention time of 50 min under these conditions; the 2-methyl structural isomer **15** exhibited a 41-min retention time.

The VPC purified material was then analyzed by 360-MHz NMR in benzene-d_6 to determine the extent of deuterium scrambling. The percent deuterium at C(2) was determined by integrating the area of the H–C(2) doublet and comparing this with the area of the H–C(5) multiplet. Table VI summarizes the primary data for deuterium scrambling; these data were used to calculate the data shown in Table I.

The optical purity of each kinetic point was determined by NMR; the sample used for determination of percent deuterium was treated with sufficient Eu(hfbc)$_3$ to split the enantiomeric C(7) methyl resonances. The optical purity was determined by integration, and the data obtained are shown in Table II.

The final measurement required for the determination of the concentrations of the four degenerate isomers was obtained by saturating the NMR samples used for determination of the optical purity with Eu(hfbc)$_3$. The NMR samples were allowed to stand with excess Eu(hfbc)$_3$ for at least 2 h; then the samples were filtered through a disposable pipet plugged with clean glass wool and deoxygenated with a slow stream of dry nitrogen for 15 min. During the course of an analysis it was sometimes necessary to subject a sample to additional deoxygenations to improve the spectrum resolution.

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Acknowledgment. We are indebted to Professor Klärner for helpful correspondence and for providing us with a copy of reference 32.

Registry No. (*S*)-**1**, 81205-75-6; (*R*)-**1**, 81205-76-7; (±)-**2**, 69268-52-6; (±)-**3**, 69268-53-7; (+)-**3**, 69268-56-0; (±)-**4**, 81205-77-8; (+)-**4**, 81205-78-9; **5**-d_0, 81205-79-0; **5**, 81205-80-3; (+)-**6**-d_0, 81205-81-4; (+)-**6**, 81218-90-8; (+)-**7**-d_0, 81205-82-5; (+) **7**, 81205-83-6; (+)-**8**-d_0, 81244-87-3; (+)-**8**, 69268-48-0; (−)-**8**, 69268-49-1; (−)-**8**-d_0, 80721-88-6; **12**, 81205-84-7; (+)-**14**, 69268-50-4; (−)-**14**, 69268-51-5; *l*-carvone, 6485-40-1; (*R*)-(−)-α-methylbenzylamine, 3886-69-9.

Interconversion of Dipoles by the Flash Vacuum Pyrolysis of Oxadiazolinones

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Abstract: The flash vacuum pyrolysis of a series of 2-phenyl-*N*-allyl-substituted 1,3,4-oxadiazolin-5-ones was investigated. The reactions can best be rationalized in terms of an initial loss of carbon dioxide to generate an *N*-allyl-substituted nitrilimine. This species undergoes a subsequent 3,3-sigmatropic shift to give a rearranged diazoalkene. The products obtained are most simply explained by invoking loss of nitrogen to generate a carbene intermediate followed by either hydrogen or vinyl migration. The formation of the 1,2-dihydronaphthalene ring can be rationalized in terms of a thermally allowed disrotatory electrocyclic reaction followed by a 1,5-sigmatropic hydrogen shift. The initially generated carbene also undergoes insertion into a neighboring methyl group to give a transient vinylcyclopropane, which is converted into a phenylcyclopentene derivative under the thermal conditions employed. The pyrolysis of *N*-benzyl-2-phenyl-1,3,4-oxadiazolinone generates a nitrilimine which rearranges to a diazoalkene via a 1,3-sigmatropic benzyl shift. Loss of nitrogen followed by a 1,2-phenyl or hydrogen migration nicely accounts for the products observed.

During the past several years, we have been engaged in a systematic study of the chemistry of nitrilium betaines, a class of 1,3-dipoles containing a central nitrogen atom and a π-bond orthogonal to the 4π-allyl system.[2a] 1,3-Dipolar cycloaddition

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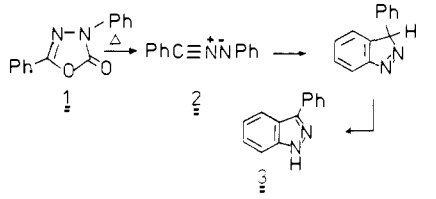
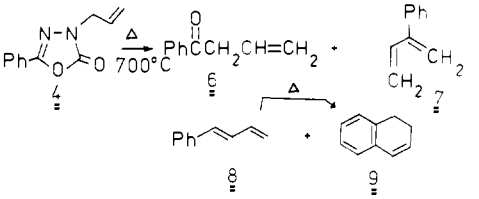
of this class of 1,3-dipoles has been widely investigated,[2b,3] and in many cases has led to the synthesis of a variety of interesting heterocyclic compounds,[4] some of which would be tedious to synthesize by other routes. In earlier papers we have shown that there are two pathways by which nitrilium betaines react with multiple π bonds.[5-8] The most frequently encountered path involves a "parallel-plane approach of addends" and can be considered to be an orbital symmetry allowed (4 + 2)-concerted process.[9,10] The other path, designated as 1,1 cycloaddition, was first encountered with nitrile ylides[11] and operates only in certain intramolecular cases. It occurs when the p orbitals of the dipolarophile have been deliberately constrained to attack perpendicular to the nitrile ylide plane. As a further consequence of our interest in this area, we thought it worthwhile to determine whether carbene-type behavior of the related nitrilimine system could also occur.[12] Access to the nitrilimine family can be realized by (a) treatment of hydrazonyl halides with base,[13] (b) thermal or photochemical decomposition of tetrazoles,[14,15] (c) photolysis of sydnones,[16] and (d) thermal elimination of carbon dioxide from 1,3,4-oxadiazolin-5-ones.[17-20] During the course of our studies, we have found that *N*-allyl-substituted nitrilimines derived from the pyrolysis of 1,3,4-oxadiazolin-5-ones undergo a novel 3,3-sigmatropic shift to give *C*-allyldiazoalkenes, which further extrude nitrogen under the reaction conditions.[21] We report here the results of these studies.

Results and Discussion

As our first model we chose to investigate the flash vacuum pyrolysis (FVP) of a series of *N*-allyl-substituted oxadiazolinones. In this technique the oxadiazolinone system is vaporized under vacuum below its decomposition temperature and then passed rapidly (with or without a low pressure of an inert carrier gas) through a hot tube. The products are collected (or trapped) on a cold finger. Thus, the use of solvents is avoided and chances of intermolecular reactions between reactive intermediates and substrate in the pyrolysis zone are minimized, favoring intramolecular (and also fragmentation) processes. Any reactive intermediates or unstable products that do survive the passage through the hot zone can react intermolecularly on the cold finger. The flash vacuum pyrolysis of the 2-phenyl-1,3,4-oxadiazolin-5-one system has been reported to be a convenient source of nitrilimines.[17-19] For example, the thermolysis of 2,4-diphenyl-1,3,4-oxadiazolin-5-one (**1**) at 500 °C gave nitrilimine **2**, which, in the absence of a trapping agent, undergoes 1,5-dipolar cyclization[22] followed by a 1,5-sigmatropic shift to produce 3-phenylindazole (**3**).[17]

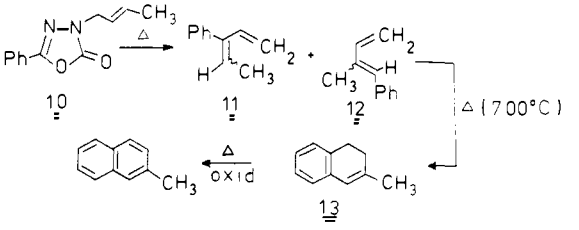


The synthesis of the desired *N*-allyloxadiazolinone was straightforward and involved the reaction of 2-phenyl-1,3,4-oxadiazolinone (**4**) with an appropriately substituted bromoalkene in the presence of base. Structural assignment of the resulting solid was made on the basis of the analytical and spectroscopic properties. Sublimation of a sample of 2-phenyl-*N*-allyl-1,3,4-oxadiazolin-5-one (**5**) through a quartz tube at 500 °C and at 10^{-2}



torr led to complete recovery of starting material, but at 700 °C (10^{-2} torr) four products were isolated in good overall yield. The major product (40%) was identified as 2-phenyl-1,3-butadiene (**7**) by comparison with an authentic sample. The two minor hydrocarbon products were identified as 1-phenyl-1,3-butadiene (**8**, 30%) and 1,2-dihydronaphthalene (**9**, 25%); in each case the material isolated was compared with independently synthesized samples. 1-Phenyl-3-buten-1-one (**6**, 5%) was isolated as the fourth product. Dihydronaphthalene **9** arises from the FVP of **8**; at 700 °C the latter was converted to **9** in high yield.

The generality of the thermolysis was investigated by studying the FVP of the corresponding *N*-2-butenyl system (**10**). Flash



vacuum pyrolysis of **10** was studied both with and without an inert carrier gas at various temperatures. At 500 °C without any nitrogen carrier gas flow, oxadiazolinone **10** was recovered. At 700 °C in a flow system, 2-methylnaphthalene **13** was the only product isolated (12%) together with some starting material (7%). When the FVP was carried out at 700 °C without a carrier gas, a 1:1 mixture of (*E*)- and (*Z*)-3-phenyl-1,3-pentadiene (**11**, 40%), 1-phenyl-2-methyl-1,3-butadiene (**12**, 20%), and 3-methyl-1,2-dihydronaphthalene (**13**, 40%) was obtained. The structures of the products were assigned by comparison with authentic samples. An authentic sample of **12** was found to afford dihydronaphthalene **13** upon pyrolysis at 700 °C.

(1) (a) John Simon Guggenheim Memorial Fellow, 1981–1982. (b) National Institutes of Health (F32-GM08052) Postdoctoral Fellow.

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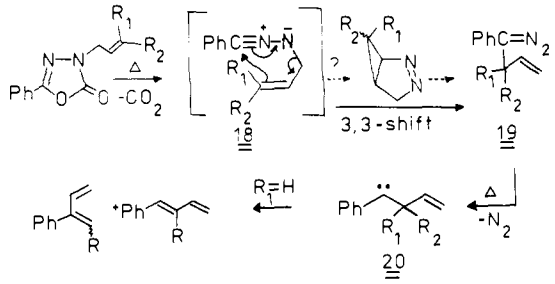
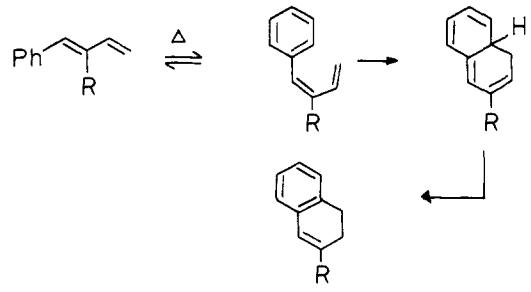
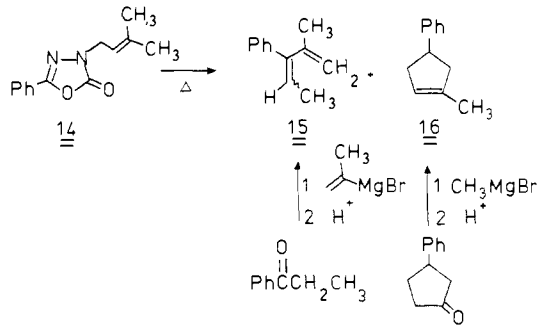
Scheme I



Scheme II

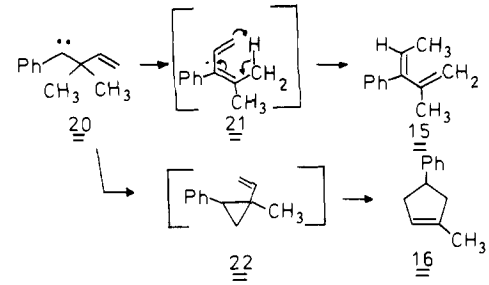


We also studied the FVP of *N*-(3-methyl-2-butenyl)oxadiazolinone **14**. Two major products were isolated from the thermolysis of this compound at 700 °C. 2-Methyl-3-phenyl-1,3-pentadiene (**15**, *E* and *Z* isomers) was the major component isolated (45%), while 1-methyl-4-phenylcyclopentene (**16**, 25%) was also found to be a significant product. An authentic sample of **16** was prepared by treating 3-phenylcyclopentanone with methylmagnesium bromide followed by dehydration of the resulting alcohol with potassium acid sulfate. Authentic 2-methyl-3-phenyl-1,3-pentadiene (1:1 *E*:*Z* mixture) was synthesized by treating propiophenone with 2-propenyl-Grignard reagent followed by an acid-catalyzed dehydration of the resulting alcohol.



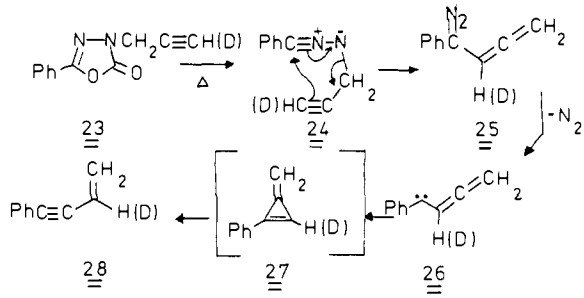
The pyrolysis results described above are interpreted mechanistically according to Scheme I. The first step involves the loss of carbon dioxide to generate an *N*-allyl-substituted nitrilimine. This species undergoes a subsequent 3,3-sigmatropic shift to give a rearranged diazoalkene (**19**). While this is written as a concerted process, it could well occur by a 1,1 cycloaddition followed by a 1,3-dipolar cycloreversion reaction.[23] The products obtained are most simply explained by invoking loss of nitrogen to generate a carbene intermediate followed by either hydrogen or vinyl migration. An alternative mechanism for generating the homoallylcarbene **20** involves an initial 3,3-sigmatropic rearrangement of the oxadiazolinone ring followed by loss of nitrogen and carbon dioxide. This path seems less likely since oxadiazolinones are known to readily lose carbon dioxide on thermolysis.[17-19] The formation of the 1,2-dihydronaphthalene ring system (Scheme II) can be rationalized by a three-step reaction sequence. The first step is an isomerization of *trans*- to *cis*-1,3-butadiene. This step is essential since only the cis isomer has the proper geometry to undergo the second step, a thermally allowed disrotatory electrocyclic reaction. The final step represents a symmetry allowed 1,5-suprafacial sigmatropic hydrogen migration, leading to restoration of the aromatic nucleus. Weber and co-workers have observed a similar reorganization in the gas-phase pyrolysis of (methoxyphenyl)-1,3-butadienes.[24]

Scheme III



The two major products obtained from the thermolysis of oxadiazolinone **14** can be explained by the sequence of reactions shown in Scheme III. The initially generated carbene **20** does not undergo a 1,2-methyl shift but rather undergoes vinyl bond migration to give **21** or insertion into the neighboring methyl group to give vinylcyclopropane **22** as a transient intermediate. Diene **21** possesses a conformational arrangement appropriate for a thermally allowed 1,5-sigmatropic shift of a hydrogen atom to give **15**. A closely related hydrogen shift has been reported to occur with 2-methyl-4-phenyl-1,3-pentadiene.[25,26] Marvell and Lin have previously demonstrated that 1-aryl-2-vinylcyclopropanes undergo facile rearrangement to cyclopentenes, thereby providing a good analogy for the isolation of cyclopentene **16**.[27] One additional point worth mentioning is that the 1,2-vinyl shift accounts for approximately 40% of the product mixture. Although vinyl groups have been reported to undergo 1,2 rearrangement to carbenes from saturated carbon centers,[28] this shift normally does not compete well with the other reactions. Perhaps the higher temperatures employed could account for the increased importance of the 1,2-vinyl shift with the above systems.

Further examples that would support the generality of these rearrangements were sought. With this in mind, we decided to prepare the *N*-propargyloxadiazolinone **23** with the expectation that this system might undergo some interesting thermal chemistry. Flash vacuum pyrolysis [700 °C (0.005 mm)] of a sample of **23** through a quartz tube gave 1-phenyl-3-buten-1-yne (**28**) as the only characterizable product in 94% isolated yield. A possible mechanism for the formation of **28** is shown below. Loss of carbon dioxide followed by a 3,3-sigmatropic shift and extrusion of ni-



(23) For a related type of rearrangement, see: Franck-Neumann, M.; Buchecker, C. *Tetrahedron Lett.* **1969**, 2659. Eaton, D. F.; Bergman, G. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 1351. Gassman, P. G.; Greenlee, W. J. *Ibid.* **1973**, *95*, 980. Welter, W.; Regitz, M. *Tetrahedron Lett.* **1975**, 1763.

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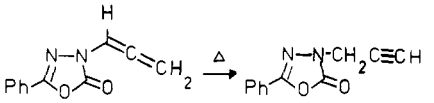
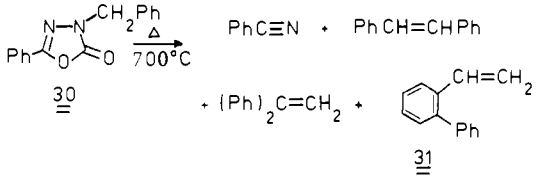
trogen would lead to allenylcarbene **26**. Cyclization of this species to methylenecyclopropene **27** followed by ring opening nicely accounts for the formation of **28**. In order to test this postulated mechanism, the corresponding deuterated propargylic compound was prepared and pyrolyzed under identical reaction conditions. If the mechanism depicted above is operative, deuterium should be found only at the C-3 position. This was borne out by experimentation; the final product obtained from the pyrolysis was fully deuterated at C-3.

We have also examined the flash vacuum pyrolysis of the isomeric allenyl oxadiazolinone **29**. This material was prepared by treating the propargylic system with a strong base followed by an acidic workup. Pyrolysis of a sample of **29** produced 1-phenyl-3-buten-1-yne (**28**) as the only characterizable product. Control experiments showed, however, that **29** is thermally unstable and rapidly rearranges to **23** at temperatures below its sublimation temperature (150 °C).



29 **23**

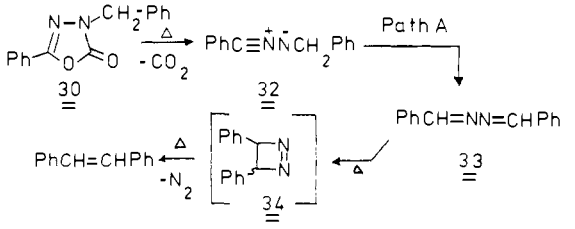
Attention was next turned to the thermal behavior of 2-phenyl-*N*-benzyl-1,3,4-oxadiazolin-5-one (**30**) so as to uncover additional information about the mechanism of these reactions, and, in particular, to attempt to obtain some evidence for the intermediacy of a diazoalkene. We are particularly interested in determining whether the nitrilimine derived from **30** would undergo a 3,3-sigmatropic rearrangement, since participation of an aromatic double bond in a Cope-type reaction seldom occurs. When the flash vacuum pyrolysis of **30** was carried out at 700 °C (10^{-2} torr), a mixture of benzonitrile (15%), *cis*- (5%) and *trans*-stilbene (42%), 1,1-diphenylethylene (12%), and *o*-phenylstyrene (**31**, 18%) was obtained. The structures of the



30 **31**

thermal products were assigned unambiguously by comparison with independently synthesized samples.

Formation of these products requires bonding, at some point in the reaction, between C-2 of the oxadiazolin-5-one ring and the benzylic carbon atom. A number of reaction sequences can be envisaged to explain these observations. One reasonable possibility to rationalize the formation of *cis*- and *trans*-stilbene (path A) involves the diazetine intermediate **34** formed from benzal azine **33**. This path parallels the 1-phenyldiaza-

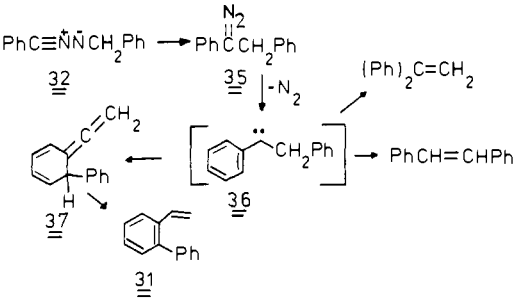


30 **32** **33** **34**

butadiene–azetidine–styrene thermal conversion reported by Wendling and Bergman.[29] Wentrup and Fischer have recently isolated an azine from the pyrolysis of 2-phenyl-*N*-methyloxadiazolin-5-one.[30] The formation of this material was suggested to involve a 1,4-hydrogen shift. A 1,4-hydrogen shift analogous to that in the conversion of **32** to **33** is also known to occur in nitrile ylides.[31]

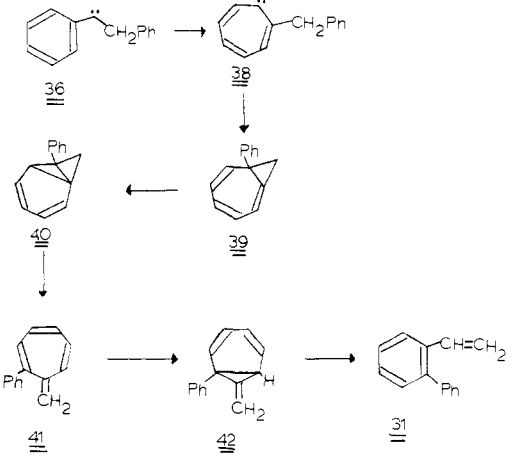
The above mechanism is relatively easy to test. Pyrolysis of an independently synthesized sample of benzal azine **33** should result in the formation of *cis*- and *trans*-stilbene. At 700 °C (10^{-2} torr), a mixture of benzonitrile (90%) and *trans*-stilbene (10%) was obtained from benzal azine. It should be noted that *trans*-stilbene is formed in much greater quantities than benzonitrile in the FVP of oxadiazolinone **30**. Although we cannot rule out the occurrence of path A, the large amount of benzonitrile formed in the thermolysis of benzal azine suggests that this route represents a minor process for the formation of the stilbenes.

The pyrolysis results described above are best interpreted by a mechanism involving the initial loss of carbon dioxide and formation of nitrilimine **32**. This species undergoes a subsequent 1,3-sigmatropic benzyl shift to give diazoalkene **35**. The products



32 **35** **36** **37** **31**

are most simply explained by invoking loss of nitrogen from **35** to generate a carbene intermediate (**36**) followed by either a hydrogen or phenyl shift. At the high temperatures employed, carbene **36** could undergo a novel 1,4-phenyl shift to give intermediate **37**, which readily tautomerizes to the observed styrene derivative. An alternate mechanism that could also rationalize the formation of *o*-phenylstyrene (**31**) involves a carbene–carbene rearrangement[32] to give cycloheptatrienyl carbene **38**. A 1,3-



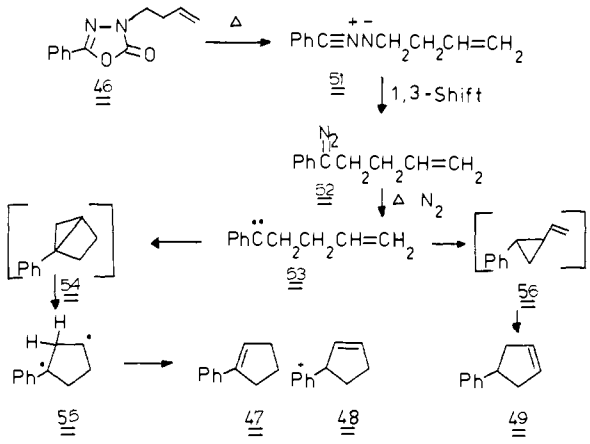
36 **38** **40** **39** **41** **42** **31**

phenyl shift followed by an electrocyclization would afford the bicyclobutane intermediate **40**. Fragmentation of the bicyclobutane bonds in the expected manner[33] will produce 1,1-diphenylethylene, as well as tetraene **41**. At the high temperatures employed, **41** would be expected to rearrange to **31**, perhaps via the intermediacy of norcaradiene **42**.

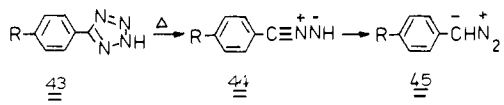
We were unable to detect a diazoalkene intermediate from the pyrolysis of oxadiazolinone **30**. Apparently, fragmentation of the diazoalkene to nitrogen and carbene **36** precludes its isolation. The independent work by Wentrup and Fischer[30] suggests that the activation energy associated with the 1,3-sigmatropic benzyl shift is lower than that for a 1,4-hydrogen shift. This would account for the variation of products obtained from the thermolysis of N-substituted oxadiazolin-5-ones. The Wentrup group has also reported results describing the pyrolytic behavior of 5-aryl-

(29) Wendling, L. A.; Bergman, R. G. *J. Org. Chem.* **1976**, *41*, 831.
(30) Fischer, S.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 502.
(31) Berstermann, H. M.; Netsch, K. P.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 503.
(32) Jones, W. M. *Acc. Chem. Res.* **1977**, *10*, 353.
(33) Closs, G. L.; Pfeffer, P. E. *J. Am. Chem. Soc.* **1968**, *90*, 2452.

Scheme IV

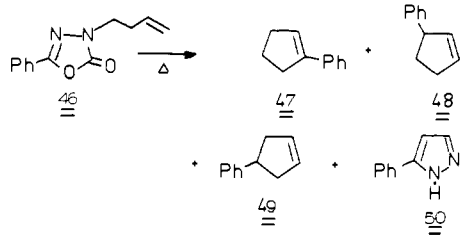


tetrazoles.[34] Thermolysis of these compounds in the gas phase results in the elimination of one molecule of nitrogen with the formation of aryldiazomethanes (**45**). When the reaction con-



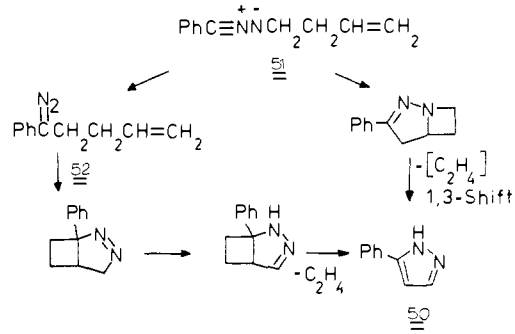
ditions were sufficiently mild, the diazoalkane can be isolated; at higher temperatures, decomposition to arylcarbenes occurred.[35] The formation of aryldiazomethanes was postulated to proceed via a 1,3-sigmatropic hydrogen shift of the initially generated nitrilimine (**43**). This sequence provides good precedent for the related 1,3-sigmatropic benzyl shift encountered with oxazolinone **30**.

In view of the stringent spatial requirements associated with the intramolecular cycloaddition reactions of nitrilium betaines,[36] we thought it worthwhile to consider what effect a variation in the spatial proximity between the dipole and dipolarophile would have on the course of the reaction. This led us to study the flash vacuum pyrolysis of the next higher homologue. Sublimation of a sample of 4-(3-butenyl)-2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (**46**) through a quartz tube at 700 °C afforded four products. The



three major hydrocarbons were identified as 1-phenyl- (**47**), 3-phenyl- (**48**), and 4-phenylcyclopentene (**49**) by comparison with independently synthesized samples. 3-Phenylpyrazole (**50**) was isolated as the fourth reaction component. We consider that the most economical explanation for the formation of the three phenyl-substituted cyclopentenes is that illustrated in Scheme IV. The initial step involves loss of carbon dioxide and generation of a nitrilimine. The observed products can then be derived from a 1,3-alkyl shift similar to that encountered with the *N*-benzyl-substituted oxadiazolinone system **30**. Loss of nitrogen from the resulting diazoalkene **52** will produce an aryl carbene, which subsequently adds across the neighboring double bond. Cleavage of the strained cyclopropyl σ bond will lead to diradical **55**, which then undergoes an internal disproportionation to give **47** and **48**. The aryl carbene can also insert into the allylic methylene bond to produce *trans*-1-vinyl-2-phenylcyclopropane (**56**). This reactive intermediate is known to rearrange to 4-phenylcyclopentene.[27]

The conversion of oxadiazolinone **46** to pyrazole **50** proceeds by an entirely different pathway. Although information on the



mechanistic details of this reaction is minimal, two tentative but reasonable paths can be advanced. One possibility involves intramolecular 1,3-dipolar cycloaddition of the nitrilimine across the neighboring π bond. The initially produced cycloadduct can then undergo loss of ethylene followed by a 1,3-hydrogen shift. An alternate path involving rearrangement of nitrilimine **51** to diazoalkene **52** followed by intramolecular 1,3-dipolar cycloaddition, a hydrogen shift, and loss of ethylene also seems possible. At the current time the available data do not distinguish between the two possibilities. Further work is necessary to establish this point.

Experimental Section[37]

Preparation of 4-Allyl-2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (4). A solution containing 4.25 g of 2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one,[38] 3.0 g of potassium hydroxide, and 9.5 g of allyl bromide in 150 mL of 95% ethanol was heated at reflux for 20 h. After cooling, the solution was diluted with an equal volume of water and extracted with chloroform. The combined extracts were washed with water and dried over magnesium sulfate. Removal of the solvent left a brown residue, which was chromatographed on a silica gel column using chloroform as the eluent to give 4.50 g (85%) of **4** as a crystalline solid: mp 58–59 °C; IR (KBr) 3.22, 3.35, 5.60, 6.20, 6.28, 6.40, 6.70, 6.93, 7.10, 7.38, 7.65, 7.78, 8.60, 9.02, 9.21, 9.40, 9.82, 10.05, 10.21, 10.70, 11.04, 12.31, 13.20, 13.80, and 14.50 μm; NMR ($CDCl_3$, 60 MHz) δ 4.39 (d, 2 H, J = 6.0 Hz), 5.1–5.5 (m, 2 H), 5.6–6.3 (m, 1 H), 7.2–7.9 (m, 5 H); ^{13}C NMR (20 MHz, $CDCl_3$) 153, 131.4, 131.2, 128.9, 125.5, 123.9, 118.9, 42.2; mass spectrum, m/e 202 (M^+, base), 129, 105, 104, and 77; UV (95% ethanol) 267 nm (ϵ 16600). Anal. Calcd for $C_{11}H_{10}N_2O_2$: C, 65.33; H, 4.98; N, 13.86. Found: C, 65.28; H, 5.03; N, 13.84.

Flash Vacuum Pyrolysis of 4. A sample containing 990 mg of **4** was distilled at 130 °C (0.05 mm) through a 20 × 0.8 cm quartz tube that was externally heated at 700 °C. The material on the dry ice cooled cold finger was taken up in chloroform. Removal of the solvent under reduced pressure left 0.62 g of a clear oil, which was chromatographed on a silica gel column using hexane as the eluent. The first fraction obtained was identified as *trans*-1-phenyl-1,3-butadiene (**8**) on the basis of its spectral properties and by comparison with an authentic sample:[39] IR (neat) 3.25, 3.27, 3.30, 6.14, 6.24, 6.71, 6.92, 7.70, 8.62, 9.40, 9.81, 10.05, 10.60, 11.20, 11.74, 13.21, and 14.20 μm; NMR ($CDCl_3$, 60 MHz) δ 5.0–5.4 (m, 2 H), 6.1–6.8 (m, 3 H), and 7.0–7.4 (m, 5 H). The second fraction isolated from the column was identified as 2-phenyl-1,3-butadiene (**7**) on the basis of its spectral properties and by comparison with an authentic sample:[40] IR (neat) 3.20, 3.24, 3.33, 5.90, 6.22, 6.29, 6.35, 6.68, 6.91, 7.92, 9.30, 9.81, 10.15, 10.92, 11.14, 12.60, and 14.20 μm; NMR ($CDCl_3$, 60 MHz) δ 5.0–5.3 (m, 3 H), 6.61 (dd, 1 H, J = 18.0 and 10.0 Hz), and 7.3 (s, 5 H). The third component isolated from the column was iden-

(34) Wentrup, C. *Helv. Chim. Acta* **1978**, *61*, 1755.
(35) Wentrup, C.; Gleiter, R.; Rettig, W. *Helv. Chim. Acta* **1974**, *57*, 2111.
(36) Padwa, A.; Ku, A. *J. Am. Chem. Soc.* **1978**, *100*, 2181.

(37) 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 Model 137 Infracord 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 on a Varian EM-390 Spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV.
(38) Golfier, M.; Milcent, R. *Bull. Soc. Chim. Fr.* **1973**, 254.
(39) Grummitt, O.; Becker, E. I. "Organic Synthesis"; Wiley: New York, 1960; Collect. Vol. 4, p 771.
(40) Shikhmamedbekova, A. Z.; Sadykh-Zade, S. I. *Azerb. Khim. Zh.* **1962**, 73.

tified as 1,2-dihydronaphthalene (**9**) by comparison with an authentic sample: IR (neat) 3.28, 3.44, 6.70, 6.88, 6.95, 7.81, 8.15, 8.29, 8.95, 9.60, 9.72, 9.90, 10.62, 11.31, 12.84, 13.50, and 14.43 μm; NMR ($CDCl_3$, 60 MHz) δ 2.0–2.4 (m, 2 H), 2.5–2.9 (m, 2 H), 5.85 (dt, 1 H, J = 10.0 and 4.0 Hz), 6.34 (dt, 1 H, J = 10.0 and 2.0 Hz) and 6.9–7.3 (m, 4 H). A control experiment showed that the flash vacuum pyrolysis of *trans*-1-phenyl-1,3-butadiene (**8**) at 700 °C produced a 1:1 mixture of *cis*-1-phenyl-1,3-butadiene and 1,2-dihydronaphthalene. The last fraction isolated from the column contained a clear oil whose structure was established as 1-phenyl-3-buten-1-one (**6**) by comparison with an authentic sample.[41]

Preparation of 4-(2-Butenyl)-2-phenyl-1,3,4-oxadiazolin-5-one (10). A 5.04-g sample of 2-phenyl-1,3,4-oxadiazolin-5-one was dissolved in 50 mL of dry dimethylformamide. To this solution was gradually added 1.55 g of a 50% sodium hydride oil dispersion. After stirring at 25 °C for 10 min, a 6.0-g sample of crotyl bromide was added. The resulting mixture was stirred at room temperature for 2 h and was then poured into water and extracted with ether. The ether extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. Molecular distillation of the residue at 130 °C (0.1 mm) gave 5.25 g (61%) of **10** as a white solid: mp 37–38 °C; IR (CCl_4) 3.25, 3.30, 3.34, 3.38, 3.45, 3.48, 5.35, 5.62, 6.19, 6.27, 6.37, 6.71, 6.92, 6.99, 7.41, 7.63, 7.75, 8.70, 8.85, 9.17, 9.73, 10.05, 10.40, 10.62, 10.81, and 11.02 μm; NMR (CCl_4, 90 MHz) δ 1.72 (d, 3 H, J = 6.0 Hz), 4.23 (m, 2 H), 5.4–6.0 (m, 2 H), 7.3–7.9 (m, 5 H); UV (95% ethanol) 267 nm (ε 16 900); mass spectrum, m/e 216 (M^+ and base), 163, 162, 157, 118, 105, and 77. Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.56; H, 5.62; N, 12.93.

Flash Vacuum Pyrolysis of 10. A 512-mg sample of **10** was distilled (0.05 mm) through a 20 × 0.8 cm quartz tube which was externally heated at 700 °C. The material on the cold finger was taken up in methylene chloride and concentrated under reduced pressure to give 310 mg of a clear oil. Preparative gas chromatography on a 1.5% OV-101 Chromosorb G column at 110 °C produced four major components. The first component isolated was identified as a mixture of (*E*)- and (*Z*)-3-phenyl-1,3-pentadiene (**11**) on the basis of its spectral properties and by comparison with an authentic sample.[42] The *E* isomer **11** showed the following spectral properties: IR (CCl_4) 3.25, 3.34, 3.48, 6.13, 6.25, 6.71, 6.94, 7.14, 7.35, 9.39, 9.80, 10.20, 10.91, 11.14, 12.04, 13.10, and 14.40 μm; NMR (CCl_4, 90 MHz) δ 1.52 (d, 2 H, J = 7.0 Hz), 4.61 (d, 1 H, J = 17.0 Hz), 4.90 (d, 1 H, J = 10.0 Hz), 5.70 (q, 1 H, J = 7.0 Hz), 6.44 (dd, 1 H, J = 17.0 and 10.0 Hz), and 6.9–7.4 (m, 5 H). Heating a sample of the *E* isomer in benzene at 80 °C for 19 h in the presence of a small amount of iodine produced a 2:1 mixture of (*E*)- and (*Z*)-3-phenyl-1,3-pentadiene. The *Z* isomer showed a doublet at δ 1.81 (3 H, J = 7.0 Hz), a doublet at 5.20 (J = 11.0 Hz), a doublet of doublets at 6.82 (J = 17.0 and 11.0 Hz), a quartet at 5.67 (J = 7.0 Hz), and a doublet at 5.06.

The second material isolated from the gas chromatographic separation was identified as 2-methyl-3,4-dihydronaphthalene (**13**) on the basis of its spectral properties and by comparison with an authentic sample:[43] IR (neat) 3.26, 3.41, 5.94, 6.09, 6.25, 6.40, 6.78, 6.99, 7.32, 7.95, 8.40, 10.05, 10.42, 11.60, 12.21, 12.60, 13.04, 13.71, and 14.40 μm; NMR (CCl_4, 90 MHz) δ 1.97 (br s, 3 H), 2.17 (br t, 2 H, J = 8.0 Hz), 2.80 (2 H, J = 8.0 Hz), 6.17 (br s, 1 H), and 6.8–7.2 (m, 4 H). The third fraction isolated was identified as 2-methylnaphthalene by comparison with an authentic sample. The fourth component isolated from the column was identified as 1-phenyl-2-methyl-1,3-butadiene (**12**) on the basis of its spectral properties and by comparison with an authentic sample:[42] IR (neat) 3.21, 3.48, 6.23, 6.71, 6.94, 7.13, 7.22, 7.39, 8.40, 8.49, 9.41, 9.50, 9.82, 10.21, 11.05, 11.21, 11.62, 12.63, 13.60, and 14.30 μm; NMR (CCl_4, 90 MHz) δ 1.90 (s, 3 H), 5.04 (d, 1 H, J = 11.0 Hz), 5.20 (d, 1 H, J = 18.0 Hz), 6.40 (s, 1 H), and 6.43 (dd, 1 H, J = 18.0 and 11.0 Hz). Flash vacuum pyrolysis of **12** at 700 °C afforded 2-methyl-3,4-dihydronaphthalene and 2-methylnaphthalene as the two major products.

Preparation of 4-(3-Methyl-2-butenyl)-2-phenyl-Δ²-1,3,4-oxadiazolin-5-one (14). To a solution containing 3.30 g oxadiazolin-5-one in 100 mL of dimethylformamide was added 1.0 g of a 50% oil dispersion of sodium hydride. After stirring for 30 min, a solution containing 4.50 g of 4-bromo-2-methyl-2-butene in 5 mL of benzene was added. The mixture was stirred at room temperature for 2 h and was then poured into 150 mL of ice water. The solution was extracted with chloroform and the organic layer was dried over magnesium sulfate. Removal of the solvent under reduced pressure left a dark oil that was chromatographed on a short silica gel column with chloroform to give **14** (4.53 g, 97%) as a crystalline solid: mp 50–51 °C; IR (KBr) 3.25, 3.33, 3.38, 5.60, 5.98, 6.20, 6.29, 6.37, 6.70, 6.92, 7.00, 7.41, 7.60, 7.72, 7.81, 8.32, 8.54, 8.70, 8.91, 9.13, 9.40, 9.72, 9.90, 10.62, 11.81, 12.40, 13.02, 13.70, and 14.30 μm; NMR ($CDCl_3$, 60 MHz) δ 1.80 (s, 6 H), 4.33 (d, 2 H, J = 7.0 Hz), 5.38 (t, 1 H, J = 7.0 Hz), 7.2–7.6 (m, 5 H); UV (95% ethanol) 267 nm (ε 17 000); mass spectrum, m/e 230 (M^+ and base), 163, 162, 149, 146, 105, and 77. Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.84; H, 6.17; N, 12.14.

Flash Vacuum Pyrolysis of 14. A 689-mg sample of **14** was distilled at 120 °C (0.05 mm) through a 20 × 0.8 cm quartz tube externally heated at 700 °C. The material on the cold finger was taken up in chloroform, and the solution was concentrated under reduced pressure to give 460 mg of a clear oil. Preparative gas chromatography on a 1.5% OV-101 Chromosorb G column at 110 °C gave a mixture of three compounds. The first major component contained a mixture of (*E*)- and (*Z*)-2-methyl-3-phenyl-1,3-pentadiene (**15**) as evidenced by its spectral properties and by comparison with an independently synthesized sample. The pure *E* isomer showed the following properties: IR (neat) 3.24, 3.42, 6.11, 6.26, 6.74, 6.94, 7.29, 8.24, 9.40, 10.03, 10.41, 10.60, 11.20, 12.14, 13.40, and 14.30 μm; NMR ($CDCl_3$, 60 MHz) δ 1.79 (s, 3 H), 1.94 (d, 3 H, J = 7.0 Hz), 4.90 (br s, 1 H), 5.28 (m, 1 H), 5.87 (q, 1 H, J = 7.0 Hz), and 7.2–7.5 (m, 5 H); UV (hexane) 244 nm (ε 22 700); mass spectrum, m/e 158 (M^+ and base), 144, 143, 129, 115, 91, and 77. A pure sample of the *Z* isomer showed the following properties: IR (neat) 3.23, 3.35, 6.17, 6.24, 6.72, 6.93, 6.98, 7.40, 7.79, 9.40, 9.81, 10.70, 11.05, 11.31, 12.14, 13.20, and 14.36 μm; NMR ($CDCl_3$, 60 MHz) δ 1.57 (d, 3 H, J = 7.0 Hz), 2.00 (s, 3 H), 4.46 (br s, 1 H), 4.92 (br s, 1 H), 5.90 (q, 1 H, J = 7.0 Hz), and 7.0–7.5 (m, 5 H); UV (hexane) 231 nm (ε 16 900); mass spectrum, m/e 158 (M^+ and base), 144, 143, 129, 115, 91, and 77.

Unequivocal proof for the structures of (*E*)- and (*Z*)-2-methyl-3-phenyl-1,3-pentadiene (**15**) was obtained by comparison with an independently synthesized sample. A solution containing 6.0 g of 2-bromopropene in 20 mL of anhydrous tetrahydrofuran was allowed to react with 0.6 g of magnesium turnings. To this mixture was added 3.35 g of propiophenone in 20 mL of tetrahydrofuran at 0 °C. After standard aqueous acid workup, 4.13 g (94%) of 2-methyl-3-phenyl-1-penten-3-ol was obtained as a clear oil; IR (neat) 2.85, 3.21, 6.09, 6.24, 6.90, 7.28, 8.50, 9.30, 9.71, 10.42, 11.13, 13.20, and 14.30 μm; NMR ($CDCl_3$, 60 MHz) δ 0.83 (t, 3 H, J = 7.0 Hz), 1.59 (br s, 3 H), 2.02 (q, 2 H, J = 7.0 Hz), 2.10 (br s, 1 H), 4.95 (q, 1 H, J = 2.0 Hz), 5.20 (br s, 1 H), and 7.1–7.5 (m, 5 H). Distillation of this material from a small quantity of potassium bisulfate hydroquinone at 100 °C (0.2 mm) afforded 3.12 g (85%) of a 1:1 mixture of (*E*)- and (*Z*)-2-methyl-3-phenyl-1,3-pentadiene (**15**).

The second major component isolated from the gas chromatography column was identified as 1-methyl-4-phenylcyclopentene (**16**) on the basis of its spectral properties and by comparison with an authentic sample:[44] bp 88–89 °C (2 mm); n^{20}_D 1.5336; IR (neat) 6.02, 11.88, and 12.45 μm; UV (95% ethanol) 262 nm (ε 300).

Preparation of 4-Propargyl-2-phenyl-Δ²-1,3,4-oxadiazolin-5-one (23). A solution containing 1.62 g of 2-phenyl-1,3,4-oxadiazolin-5-one in 20 mL of dimethylformamide was treated with 0.7 g of a 50% oil dispersion of sodium hydride. After stirring at 25 °C for 30 min, a solution containing 2.0 g of propargyl bromide in 5 mL of dimethylformamide was added. The mixture was stirred at 25 °C for 2 h and was poured into 150 mL of ice water. The precipitate that formed was collected and recrystallized from chloroform–hexane to give 1.92 g (96%) of **23** as a white solid, mp 123–124 °C; IR (KBr) 3.03, 3.35, 5.64, 6.23, 6.29, 6.40, 6.75, 6.96, 7.12, 7.26, 7.40, 7.46, 7.68, 8.80, 9.40, 9.91, 10.80, 12.30, 13.81, 14.15, and 14.40 μm; NMR ($CDCl_3$, 60 MHz) δ 2.40 (t, 1 H, J = 2.0 Hz), 4.51 (d, 2 H, J = 2.0 Hz), 7.1–7.8 (m, 5 H); UV (95% ethanol) 263 nm (ε 17 200); mass spectrum, m/e 200 (M^+ and base), 128, and 77. Anal. Calcd for $C_{11}H_8N_2O_2$: C, 65.99; H, 4.03; N, 13.99. Found: C, 65.87; H, 4.08; N, 13.92.

Flash Vacuum Pyrolysis of 23. A 772-mg sample of **23** was sublimed at 100 °C (0.05 mm) through a 20 × 0.8 cm quartz tube externally heated at 700 °C. The material which condensed on the cold finger was removed with chloroform. The organic solvent was removed under reduced pressure to leave behind 469 mg of a clear oil. Molecular distillation of this oil at 120 °C (0.01 mm) gave 1-phenyl-3-buten-1-yne (**28**) as a clear oil; IR (neat) 3.21, 3.40, 4.51, 4.59, 6.24, 6.26, 6.31, 6.74, 6.96, 7.11, 7.79, 7.86, 7.98, 9.40, 9.80, 10.41, 11.04, 13.42, and 14.31 μm; NMR ($CDCl_3$, 90 MHz) δ 5.48 (dd, 1 H, J = 10.0 and 3.0 Hz), 5.68 (dd, 1 H, J = 18.0 and 3.0 Hz), 6.00 (dd, 1 H, J = 18.0 and 10.0 Hz), and 7.1–7.5 (m, 5 H); UV (hexane) 281, 264, 259, and 254 nm (ε 31 100, 14 000, 13 300, and 13 200); mass spectrum, m/e 128 (M^+ and base),

(41) Trahanovsky, W. S.; Macaulay, D. B. *J. Org. Chem.* **1973**, *38*, 1497.
(42) Alder, K.; Haydn, J.; Heinbach, K.; Neufang, K. *Liebigs Ann. Chem.* **1954**, *586*, 110.
(43) Kaubisch, N.; Daly, J. W.; Jerina, D. M. *Biochemistry* **1972**, *11*, 3080.
(44) Kolobielski, M.; Pines, M. *J. Am. Chem. Soc.* **1957**, *79*, 5820.

127, and 102. Anal. Calcd for $C_{10}H_8$: C, 93.71; H, 6.29. Found: C, 93.62; H, 6.36.

The structure of **28** was unambiguously established by comparison with an authentic sample prepared according to the procedure of Hagahara.[45]

A sample of 4-(3-propyn-*1*-d_1-3-yl)-2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (**23**-*d*) was prepared by reacting 2-phenyl-1,3,4-oxadiazolin-5-one with propargyl-*1*-d_1 bromide;[46] NMR of **23**-*d* ($CDCl_3$, 90 MHz) δ 4.59 (s, 2 H), 7.1–7.8 (m, 5 H). Flash vacuum pyrolysis of this material at 700 °C afforded 1-phenyl-3-deuterio-3-buten-1-yne (**28**-*d*) as the major product; NMR (90 MHz, $CDCl_3$) δ 5.49 (dt, 1 H, J = 3.0 and 1.5 Hz), 5.80 (dt, 1 H, J = 3.0 and 2.7 Hz), and 7.2–7.6 (m, 5 H).

Preparation and Thermolysis of 4-Allenyl-2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (29). To a solution containing 0.32 g of **23** in 12 mL of dimethylformamide was added 0.14 g of oil-free sodium hydride. The reaction mixture was allowed to stir for 3 h and was then poured into 80 mL of ice water. The solid that precipitated was filtered and recrystallized from hexane to give 0.35 g (88%) of the rearranged allene isomer **29**: mp 105–106 °C; IR (KBr) 3.28, 5.68, 6.10, 6.16, 6.94, 7.26, 7.48, 7.58, 9.96, and 11.50 μm; NMR ($CDCl_3$, 60 MHz) δ 5.65 (d, 2 H, J = 6.0 Hz), 6.85 (t, 1 H, J = 6.0 Hz), 7.2–7.5 (m, 3 H), and 7.7–7.9 (m, 2 H); UV (95% ethanol) 277 nm (ϵ 17 400); mass spectrum, m/e 200 (M^+ and base), 128, and 77. Anal. Calcd for $C_{11}H_8N_2O_2$: C, 65.99; H, 4.03; N, 13.99. Found: C, 65.90; H, 4.03; N, 13.97.

Flash vacuum pyrolysis of a 300-mg sample of oxadiazolinone **29** through a quartz tube heated at 700 °C (10^{-2} torr) afforded 1-phenyl-3-buten-1-yne (**28**) as the exclusive product. Analysis of the unflashed residue which remained in the pot indicated that the 4-allenyloxadiazolinone **29** had completely rearranged to the corresponding propargylic isomer at 110 °C.

Preparation of 4-Benzyl-2-phenyl-Δ^2-1,34-oxadiazolin-5-one (30). To a solution containing 1.62 g of 2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one in 40 mL of dimethylformamide was added 0.48 g of oil-free sodium hydride. The reaction mixture was allowed to stir at 25 °C for 1 h, and then a solution containing 1.88 g of benzyl bromide in 2 mL of dimethylformamide was added. The resulting mixture was allowed to stir at room temperature for 4 h and was then poured into 80 mL of an ice–water mixture. The solid which formed was collected and recrystallized from benzene to give **30** as a white solid (85%): mp 118–119 °C; IR (CCl_4) 5.57, 6.67, 6.87, 7.35, 9.80, 14.18, and 14.49 μm; NMR ($CDCl_3$, 90 MHz) δ 4.9 (s, 2 H) and 7.2–7.9 (m, 5 H); mass spectrum, m/e 252 (M^+ and base), 105, 92, and 77; UV (95% ethanol) 267 nm (ϵ 16 700). Anal. Calcd for $C_{15}H_{12}N_2O_2$: C, 71.41; H, 4.80; N, 11.11. Found: C, 71.34; H, 4.82; N, 11.06.

Flash Vacuum Pyrolysis of 30. A sample containing 1.0 g of **30** was distilled at 125 °C (0.05 mm) through a 20 × 0.8 cm quartz tube which was externally heated to 700 °C. The material on the dry ice cooled cold finger was taken up in methylene chloride. Removal of the solvent under reduced pressure left 0.84 g of a clear oil which was chromatographed on a silica gel column using hexane as the eluent. The major components isolated corresponded to benzonitrile (15%), *cis*- and *trans*-stilbene (5 and 42%), 1,1-diphenylethylene (12%), and *o*-phenylstyrene (**31**) (18%). The identity of these compounds was established by comparison with authentic samples. A pure sample of **31**[47,48] was prepared by the sodium borohydride reduction of *o*-phenylacetophenone followed by dehydration with potassium bisulfate: bp 125 °C (5 mm); NMR (90 MHz, $CDCl_3$) δ 5.18 (dd, 1 H, J = 15.0 and 2.0 Hz), 5.65 (dd, 1 H, J = 18.0 and 2.0 Hz), 6.71 (dd, 1 H, J = 18.0 and 15.0 Hz), and 7.2–7.8 (m, 9 H); UV (95% ethanol) 232 and 253 nm (ϵ 21 000 and 15 500).

Preparation of 4-(3-Butenyl)-2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (46). To a solution containing 5.0 g of oxadiazolin-5-one in 50 mL of dimethylformamide was added 1.55 g of a 50% oil dispersion of sodium hydride. The resulting suspension was stirred for 30 min at room temperature, and then 4.8 g of 4-bromo-1-butene was added. After stirring at 25 °C for 3 h, the mixture was poured into water and extracted with ether. The ether layer was dried over magnesium sulfate and the solvent was removed under reduced pressure. The resulting residue was distilled at 140 °C (0.1 mm) to give 5.13 g (59%) of **46** as a white solid: mp 37–38 °C; IR (CCl_4) 3.22, 3.33, 3.39, 3.50, 5.60, 6.10, 6.21, 6.27, 6.35, 6.69, 7.19, 7.41, 7.52, 7.63, 7.75, 8.03, 8.51, 8.97, 9.05, 9.17, 9.39, 9.66, 9.90, 10.93, and 14.70 μm; NMR (CCl_4, 90 MHz) δ 2.50 (q, 2 H, J = 8.0 Hz), 3.78 (t, 2 H, J = 8.0 Hz), 5.07 (dd, 1 H, J = 10.0 and 1.0 Hz), 5.10 (dd, 1 H, J = 18.0 and 1.0 Hz), 5.80 (ddt, 1 H, J = 18.0, 10.0, and 8.0 Hz), and 7.3–7.9 (m, 5 H); UV (95% ethanol) 267 nm (ϵ 17 500); mass spectrum, m/e 216 (M^+ and base), 163, 162, 118, 105, and 77. Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.49; H, 5.67; N, 12.89.

Flash Vacuum Pyrolysis of 46. A 1.46-g sample of **46** was slowly distilled at 130 °C (0.05 mm) through a 20 × 0.8 cm quartz tube which was externally heated at 700 °C. The material that condensed on the cold finger was taken up in methylene chloride. Removal of the solvent left 736 mg of a yellow oil, which was chromatographed on a silica gel column with hexane as the eluent. The first fraction isolated contained a clear oil whose structure was established as 3-phenylcyclopentene (**48**) on the basis of its spectral properties and by comparison with an authentic sample:[49] IR (neat) 3.27, 3.40, 6.25, 6.71, 6.90, 7.35, 9.30, 9.71, 9.90, 10.92, 13.24, and 14.50 μm; NMR (CCl_4, 90 MHz) δ 1.5–2.0 (m, 1 H), 2.3–2.7 (m, 3 H), 3.7–4.0 (m, 1 H), 5.81 (td, 1 H, J = 5.0 and 1.5 Hz), 5.92 (td, 1 H, J = 5.0 and 1.5 Hz), and 7.0–7.4 (m, 5 H). The second fraction corresponded to 1-phenylcyclopentene (**47**) which was assigned on the basis of its spectral properties and by comparison with an authentic sample:[50] IR (neat) 3.23, 3.50, 6.10, 6.27, 6.37, 6.71, 7.49, 7.58, 7.75, 8.06, 9.41, 9.72, 10.51, 11.10, 12.40, 13.42, and 14.60 μm; NMR (CCl_4, 90 MHz) δ 2.03 (p, 2 H, J = 7.0 Hz), 2.3–2.8 (m, 4 H), 6.0–6.2 (m, 1 H), and 7.0–7.6 (m, 5 H). The third fraction corresponded to a clear oil whose structure was assigned as 4-phenylcyclopentene (**49**) on the basis of its spectral properties and by comparison with an authentic sample:[27] IR (CCl_4) 3.25, 3.40, 3.50, 6.25, 6.71, 6.90, 6.94, 7.46, 9.35, 9.76, 10.60, and 11.10 μm; NMR (CCl_4, 90 MHz) δ 2.40 (dd, 2 H, J = 15.0 and 8.0 Hz), 2.80 (dd, 2 H, J = 15.0 and 8.0 Hz), 3.40 (p, 1 H, J = 8.0 Hz), 5.73 (s, 1 H), and 7.0–7.3 (m, 5 H). A sample of 1-phenyl-2-vinylcyclopropane (**56**)[27] [NMR (CCl_4, 90 MHz) δ 1.02 (td, 1 H, J = 9.0 and 6.0 Hz), 1.20 (ddd, 1 H, J = 6.0 Hz), 1.5–2.0 (m, 1 H), 4.7–5.2 (m, 3 H), and 7.0–7.4 (m, 5 H)] was subjected to flash vacuum pyrolysis at 700 °C. The only material isolated from the cold finger was **49**.

The last fraction isolated from the silica gel chromatography column contained a yellow solid (90 mg), mp 76–77 °C, whose structure was established as 3-phenylpyrazole (**50**) on the basis of its spectral properties and by comparison with an authentic sample:[51] IR (KBr) 3.14, 3.25, 3.36, 3.41, 3.50, 6.21, 6.69, 6.80, 6.90, 6.97, 7.43, 7.66, 7.75, 7.87, 8.33, 9.05, 9.17, 9.43, 9.66, 10.60, 10.91, 11.60, and 14.70 μm; NMR ($CDCl_3$, 90 HHz) δ 6.47 (d, 1 H, J = 2.0 Hz), 7.1–7.4 (m, 3 H), 7.48 (d, 1 H, J = 2.0 Hz), 7.5–7.8 (m, 2 H), and 13.4 (br s, 1 H).

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