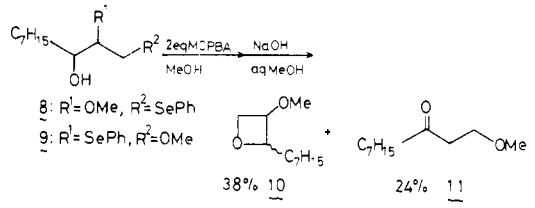
rification by silica gel chromatography. The use of ketone enolates or their lithiated *N,N*-dimethylhydrazone derivatives resulted in the formation of complex mixtures.

There is a reported example of lactone formation from 5-(phenylseleno)valeric acid via oxidative elimination with hydrogen peroxide.[14] Related phenomena appear to direct the present ring-closure reaction. Thus, a mixture of hydroxy selenides **8** and **9** (ca. 1:1), prepared from 1-decen-3-ol via oxyselenation,[15] was treated with MCPBA (2 equiv) followed by sodium hydroxide in aqueous methanol to give the corresponding oxetane **10** and 1-methoxy-3-decanone **11**[16] in 38% and 24% yields, respectively. This observation supports the proposed conjugate addition of methoxide anion followed by ring closure through elimination of the selenium moiety.[17]



The following procedure is representative for the preparation of 3-methoxyoxetanes.

3-Methoxy-2-(2-phenylethyl)oxetane. To a solution of (*E*)-3-(phenylseleno)-2-propenal (106 mg, 0.5 mmol) in THF (5 mL) was added a THF solution of 2-(phenylethyl)magnesium chloride (0.77 mL of a 0.78 M solution, 0.6 mmol) at 0 °C. After workup with saturated NH_4Cl followed by drying and concentration, the crude oil was treated with 85% MCPBA (206 mg, 1.0 mmol) in methanol (5 mL) at room temperature for 30 min. Then a 1 M aqueous solution of sodium methoxide[18] (2 mL) was added to the reaction mixture and it was stirred for 18 h at room temperature. Workup with saturated aqueous NaCl followed by extraction with ether, drying, and concentration gave the crude product as an oil, which was purified by preparative TLC to afford the title compound (77 mg, 80%) as a colorless oil.

In conclusion, the easily accessible compound, 3-(phenylseleno)-2-propenal, is an efficient reagent for the formation of oxetane rings and for the introduction of the three-carbon unit into various nucleophiles. We are currently studying the application of this reaction to bicyclic systems together with its precise scope and limitations.

Registry No. (*E*)-**2** (Ar = Ph), 74824-70-7; (*Z*)-**2** (Ar = Ph), 74824-71-8; (*Z*)-**2** (Ar = *p*-ClC_6H_4), 74824-72-9; (*E*)-**3** (Ar = Ph; R = $C_6H_5CH_2CH_2$), 74824-73-0; (*Z*)-**3** (Ar = Ph; R = $C_6H_5CH_2CH_2$), 74824-74-1; (*E*)-**3** (Ar = *p*-ClC_6H_4; R = $C_6H_5(CH_2)_2$), 74824-75-2; (*Z*)-**3** (Ar = *p*-ClC_6H_4; R = $C_6H_5(CH_2)_2$), 74824-76-3; (*E*)-**3** (Ar = Ph; R = $C_{10}H_{21}$), 74824-77-4; (*Z*)-**3** (Ar = Ph; R = $C_{10}H_{21}$), 74824-78-5; (*E*)-**3** (Ar = Ph; R = C_6H_{13}), 74835-30-6; (*Z*)-**3** (Ar = Ph; R = C_6H_{13}), 74835-31-7; (*E*)-**3** (Ar = *p*-ClC_6H_4; R = Ph), 74824-79-6; (*Z*)-**3** (Ar = *p*-ClC_6H_4; R = Ph), 74824-80-9; (*E*)-**3** (Ar = R = Ph), 74824-81-0; (*Z*)-**3** (Ar = R = Ph), 74824-82-1; **3** (Ar = Ph; R = $C_5H_{11}CHCO_2C(CH_3)_3$), 74824-83-2; **3** (Ar = Ph; R = $C_4H_9CHCO_2C(CH_3)_3$), 74835-32-8; **4a** (R = $C_6H_5CH_2CH_2$), 74824-84-3; **4b** (R = $C_6H_5CH_2CH_2$), 74824-85-4; **4a** (R = $C_{10}H_{21}$), 74824-86-5; **4b** (R = $C_{10}H_{21}$), 74824-87-6; **4a** (R = C_6H_{13}), 74824-88-7; **4b** (R = C_6H_{13}), 74824-89-8; **4a** (R = C_6H_5), 74824-90-1; **4b** (R = C_6H_5), 74824-91-2; **4a** (R = $C_5H_{11}CHCO_2C(CH_3)_3$), 74824-92-3; **5**, 74824-93-4; **6**, 74824-94-5; **7**, 74824-95-6; **8**, 74824-96-7; **9**, 74824-97-8; **10**, 74824-98-9; **11**, 74835-33-9; $C_6H_5CH_2CH_2Cl$, 622-24-2; $C_{10}H_{21}Br$, 112-29-8; $C_6H_{13}Br$, 111-25-1; C_6H_5Br, 108-86-1; C_6H_5Li, 591-51-5; $C_5H_{11}CHLiCO_2C(CH_3)_3$, 74835-34-0; **4a** (R = $C_4H_9CHCO_2C(CH_3)_3$), 74824-99-0; $LiCH_2CO_2$-*t*-Bu, 41850-36-6; lithium γ-valerolactone enolate, 74825-00-6; *tert*-butyl hexanoate, 2492-18-4.

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Received May 27, 1980

Flash Vacuum Pyrolysis of *N*-Allyl-Substituted 1,3,4-Oxadiazolin-5-ones

Summary: The flash vacuum pyrolysis of several *N*-allyl-substituted 1,3,4-oxadiazolin-5-ones generates nitrile imines which rearrange to diazoalkenes via a 3,3-sigmatropic shift.

Sir: The cycloaddition of 1,3-dipoles has become an important method for the synthesis of five-membered heterocyclic rings.[1] One of the more interesting members of the 1,3-dipole family is the nitrile imines.[2] This class of dipoles has traditionally been prepared by the thermal decomposition of tetrazoles,[3,4] the photolysis of sydnones,[5] or the base-induced elimination of hydrogen halide from hydrazonyl halides.[6] Recently, it has been shown that 1,1-intramolecular cycloaddition of nitrile imines can compete with the normal 1,3-addition when certain geometric constraints are imposed.[7,8] In these cases, the reactions can be formulated in terms of the carbene form of the dipole. Because of the theoretical[9] and experimental challenge of nitrile imine cycloaddition,[10] we subjected a series of *N*-allyl-1,3,4-oxadiazolin-5-ones to flash vacuum thermolysis[11] in the hope of obtaining additional examples of 1,1-cycloaddition. We have found that *N*-allyl-substituted nitrile imines derived from the pyrolysis undergo a novel 3,3-sigmatropic shift to give *C*-allyl diazoalkenes which further extrude nitrogen under the reaction conditions.

Sublimation of a sample of 2-phenyl-*N*-allyl-1,3,4-oxadiazolin-5-one (**1**) through a quartz tube at 500 °C and at 10^{-2} torr led to complete recovery of starting material, but

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(16) For formation of the ketone via a related reaction, see: Takahashi, T.; Nagashima, H.; Tsuju, J. *Tetrahedron Lett.* **1978**, 799; Reich, H. J.; Chow, F.; Shah, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 6638; Shah, S. K.; Chow, F. *Ibid.* **1979**, *101*, 6648.
(17) For evidence of S_N2 displacement of the arylselenino group, see ref 6.
(18) When ester or lactone enolates were employed, lithium hydroxide was used in place of sodium hydroxide. This may prevent retro-Reformatsky reactions.

(1) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes", S. Patai, Ed., Interscience, New York, 1964, p 806.
(2) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565, 633 (1963).
(3) R Huisgen, M. Seidel, J. Sauer, J. W. McFarland, and G. Wallbillich, *J. Org. Chem.*, **24**, 892 (1959); J. S. Clover, A. Eckell, R. Huisgen, and R. Sustmann, *Chem. Ber.*, **100**, 60 (1967).
(4) P. Scheiner and J. F. Dinda, Jr., *Tetrahedron*, **26**, 2619 (1970); P. Scheiner and W. M. Litchman, *J. Chem. Soc., Chem. Commun.*, 781 (1972).
(5) M. Marky, H. Meier, A. Wunderli, H. Heimgartner, H. Schmid, and H. J. Hansen, *Helv. Chim. Acta*, **61**, 1477 (1978).
(6) R. Huisgen, M. Seidel, G. Wallbillich, and H. Knupfer, *Tetrahedron*, **17**, 3 (1962).
(7) L. Garanti, A. Vigevami, and G. Zecchi, *Tetrahedron Lett.*, 1527 (1976); L. Garanti and G. Zecchi, *J. Chem. Soc., Perkin Trans. 1*, 2092 (1977).
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(10) N. H. Toubro and A. Holme, *J. Am. Chem. Soc.*, **102**, 2093 (1980).
(11) The flash vacuum thermolysis of 1,3,4-oxadiazolin-5-ones has been reported to extrude carbon dioxide and generate nitrile imines; see C. Wentrup, A. Damerius, and W. Reichen, *J. Org. Chem.*, **43**, 2037 (1978).

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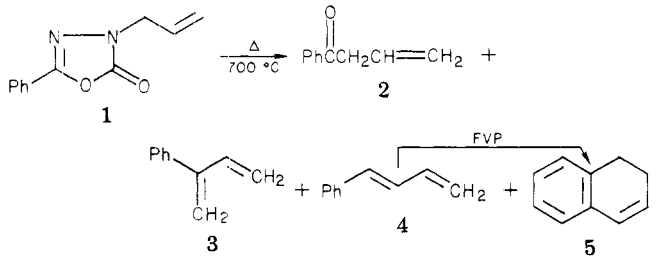
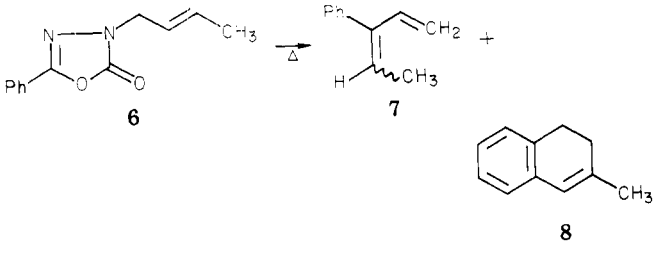
at 700 °C (10^{-2} torr) four products were isolated in good overall yield. The major product (40%) was identified as 2-phenyl-1,3-butadiene (**3**) by comparison with an authentic sample. The two minor hydrocarbon products



1 2 3 4 5

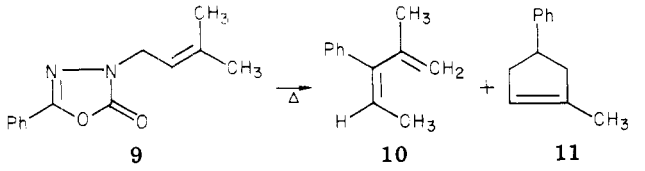
were identified as 1-phenyl-1,3-butadiene (**4**, 30%) and 1,2-dihydronaphthalene (**5**, 25%): in each case the material isolated was compared with independently synthesized samples. 1-Phenyl-3-buten-1-one (**2**, 5%) was isolated as the fourth product. Dihydronaphthalene **5** arises from the FVP of **4**; at 700 °C the latter was converted to **5** in high yield.

The generality of the thermolysis was investigated by studying the FVP of the corresponding *N*-2-butenyl system **6**. Flash vacuum pyrolysis of oxadiazolinone **6** at 700 °C gave a 40% yield of a 1:1 mixture of (*E*)- and (*Z*)-3-phenyl-1,3-pentadiene (**7**) as well as 3-methyl-1,2-dihydronaphthalene (**8**, 40%). The structures of the products were assigned unambiguously by comparison with authentic samples.



6 7 8

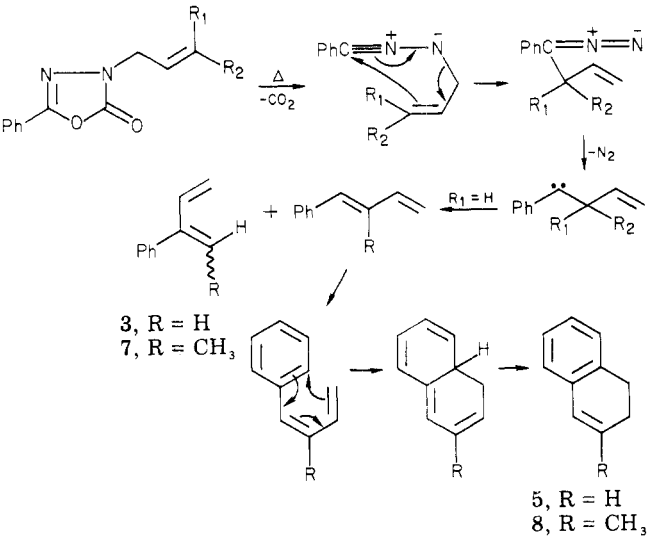
We also studied the FVP of *N*-(3-methyl-2-butenyl)oxadiazolinone **9**. Two major products were isolated from the thermolysis of this compound at 700 °C. 2-Methyl-3-phenyl-1,3-butadiene (**10**) was the major component isolated (45%) while 4-phenyl-1-methylcyclopentene (**11**) was also found to be a significant product, this being isolated in 25% yield.



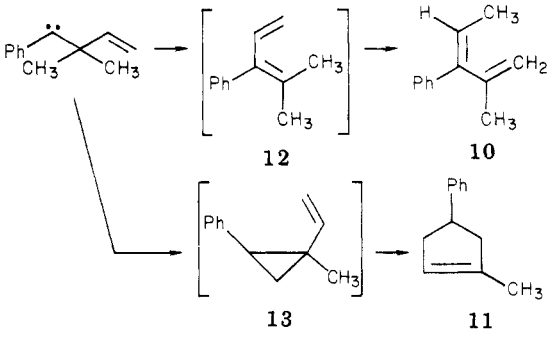
9 10 11

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 nitrile imine. 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[12] The formation of the 1,2-dihydronaphthalene ring system can be rationalized by a three-step reaction sequence.[13] The first step is an isomerization of *trans*- to

Scheme I



Scheme II

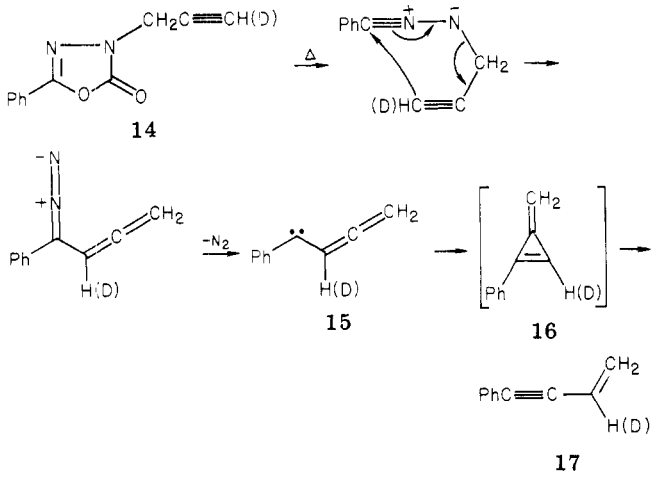


cis-1,3-butadiene. This step is essential since only the cis isomer has the proper geometry to undergo the second step, a thermally allowed disrotatory electrocyclic reaction. The final step represents a symmetry allowed 1,5-suprafacial sigmatropic hydrogen migration, leading to restoration of the aromatic nucleus.

The two major products obtained from the thermolysis of oxadiazolinone **9** can be explained by the sequence shown in Scheme II. The initially generated carbene may undergo vinyl bond migration to give **12** or insert into the neighboring methyl group to give vinylcyclopropane **13** as a transient intermediate. Diene **12** possesses a conformational arrangement appropriate for a thermally allowed [1,5]-sigmatropic shift of a hydrogen atom to give **10**.[14] Marvell and Lin have previously demonstrated that 1-aryl-2-vinylcyclopropanes undergo facile rearrangement to cyclopentenes, thereby providing good analogy for the isolation of **11**.[15]

Further examples which would support the generality of these rearrangements were sought. With this in mind, we decided to prepare the *N*-propargyloxadiazolinone **14** with the expectation that this system might undergo some interesting thermal chemistry. Flash vacuum pyrolysis (700 °C at 0.005 mm) of a sample of **14** through a quartz tube gave 1-phenyl-3-buten-1-yne[16] (**17**) as the only characterizable product in 94% isolated yield. A possible mechanism for the formation of **17** is shown below. Loss

(12) An alternate mechanism for generating the homoallylcarbene involves an initial 3,3-sigmatropic rearrangement followed by loss of nitrogen and carbon dioxide.
(13) M. R. Radcliffe and W. P. Weber, *J. Org. Chem.*, **42**, 297 (1977).
(14) A large number of such rearrangements are known; see R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, 1970, Chapter 7.
(15) E. N. Marvell and C. Lin, *J. Am. Chem. Soc.*, **100**, 877 (1978).
(16) K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, 4467 (1975).



14 15 16 17

of carbon dioxide followed by a 3,3-sigmatropic shift and extrusion of nitrogen would lead to allenylcarbene **15**. Cyclization of this species to methylenecyclopropene **16** followed by ring opening nicely accounts for the formation of **17**. 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.

In summary, all the oxadiazolinones investigated gave products which were consistent with a 3,3-sigmatropic shift of an *N*-allyl-substituted nitrile imine to a *C*-allyl-substituted diazoalkene. A mechanism involving loss of nitrogen and generation of a carbene intermediate provides a common rationalization for the diversity of products formed.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health.

Registry No. 1, 55084-88-3; 2, 6249-80-5; 3, 2288-18-8; (*E*)-4, 16939-57-4; (*Z*)-4, 31915-94-3; 5, 447-53-0; 6, 74752-47-9; (*E*)-7, 70178-90-4; (*Z*)-7, 64035-02-5; 8, 2717-44-4; 9, 74752-48-0; 10, 74752-49-1; 11, 74752-50-4; 12, 74752-51-5; 13, 74752-52-6; 14, 74752-53-7; 15, 74752-54-8; 16, 74752-55-9; 17, 13633-26-6.

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Received June 4, 1980

Homologation of Organoboranes via Carbonylation-Reduction

Summary: Reduction by lithium aluminum hydride of the intermediate formed in the hydride-induced carbonylation of *B*-R-9-BBN provides a valuable new method for the stereospecific homologation of *B*-R-9-BBN → *B*-RCH_2-9-BBN (R = alkyl, cycloalkyl, bicycloalkyl). Since these derivatives are versatile intermediates for organic synthesis, readily transformed into a variety of products, this development makes available a valuable new route to homologated derivatives.

Sir: The utility of boranes in organic synthesis stems in large part from the high regio- and stereoselectivity of their transformations. Application of this chemistry hinges on the availability of regio- and stereochemically pure organoboranes, which in turn is limited by the selectivity of the hydroboration reaction and/or by the availability of the requisite olefin (or alkyne).

Table I. Homologation of *B*-R-9-BBN via Carbonylation-Reduction

R of *B*-R-9-BBN[a]	*B*-RCH_2-9-BBN	yield,[b] %	δ[c]
n-octyl	2	70	81.7
cyclohexyl	4	85	88.2
cyclopentyl	6	65	88.8
cyclooctyl	8	75	84.5
exo-2-norbornyl	12	77	87.3
trans-2-methylcyclopentyl	15	88	87.5

[a] *B*-R-9-BBN was made in situ from 9-BBN and a small excess of the alkene. [b] Distilled yields based on 9-BBN. [c] ^{11}B NMR chemical shifts are relative to $BF_3 \cdot OEt_2$ (δ 0) with chemical shifts downfield assigned as positive.

As part of an ongoing interest in the synthesis of boranes not available via hydroboration,[1] we desired a convenient method for the homologation of organoboranes. Because of the demonstrated usefulness of 9-BBN and its derivatives, a general synthesis of *B*-(alkylmethyl)-9-BBN compounds would be of especial interest. Previous results[2] from a study of the hydride-induced carbonylation of organoboranes[3] suggested that hydride reduction of the intermediate (which provides aldehydes and methylol derivatives upon oxidation and hydrolysis, respectively) might provide a convenient route to these derivatives.

Indeed, we have found that carbonylation of *B*-alkyl-9-BBN, followed by reduction of the intermediate, provides a high-yield, stereospecific synthesis of the homologous borane. Strict temperature control during both steps is crucial for success. Thus, carbonylation[4] at −20 °C in the presence of 1.3 equiv of freshly prepared lithium trimethoxyaluminum hydride (LTMA), reduction at the same temperature[5] with 1.0 molar equiv of lithium aluminum hydride,[6] and hydrolysis of the borohydride formed[7] provides the product in 70–90% distilled yields. The purity is quite high, 97–100% by GLC.[8]

Difficulties were encountered initially in isolating the product from the gelatinous aluminum byproducts until it was found that addition of methanesulfonic acid provides a fine granular precipitate which is easily centrifuged from the reaction mixture, leaving a clear supernatant. This is decanted, concentrated, and distilled to give the product. Table I shows the scope of the process.

For instance, straight-chain alkyl groups can be lengthened by one carbon atom, as shown below for *B*-*n*-octyl-9-BBN (**1**, formed in situ via hydroboration of the readily available 1-octene).

The sequence is also effective for cyclic olefins as substrates, yielding the *B*-cycloalkylmethyl derivatives in good yield.

(1) (a) Kramer, G. W.; Brown, H. C. *J. Organomet. Chem.* **1974**, *73*, 1. (b) Brown, H. C.; Sinclair, J. A. *Ibid.* **1977**, *131*, 163. (c) Molander, G. A. Ph.D. Thesis, Purdue University, 1979.

(2) Coleman, R. A.; Hubbard, J. L., unpublished results.

(3) (a) Brown, H. C.; Coleman, R. A.; Rathke, M. W. *J. Am. Chem. Soc.* **1968**, *90*, 499. (b) Brown, H. C.; Knights, E. F.; Coleman, R. A. *Ibid.* **1969**, *91*, 2144. (c) Brown, H. C.; Hubbard, J. L.; Smith, K. *Synthesis* **1979**, 701.

(4) All carbonylations were performed in an automatic gasimeter available from Ace Glass Inc.

(5) Lack of temperature control at this stage causes loss of product due to dealkylation (exchange with AlH_3).

(6) Two equivalents of $Li(MeO)_3AlH$ is also effective; this provides for 2-carbon homologation of olefins to primary aldehydes via a second carbonylation, followed by oxidation.

(7) Brown, H. C.; Hubbard, J. L.; Singaram, B. *J. Org. Chem.* **1979**, *44*, 5004.

(8) The products were characterized via oxidation to the corresponding methylol derivatives, which were available from the previous study.[3c]

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