is the only one in the literature mentioning the compound. They obtained it as a byproduct from the acetolysis of a 3β-(tosyloxy)-5α-androstane-7,17-dione. Only an elemental analysis was given in support of the structural assignment.

We undertook the resynthesis of 5α-androst-2-ene-7,17-dione to verify both the structure and the measurement. We used dehydroepiandrosterone (3β-hydroxyandrost-5-en-17-one) as the starting material and followed this scheme: esterification of the 3β-alcohol function; allylic oxidation at C-7 with a chromium trioxide–3,5-dimethylpyrazole complex;[6] hydrogenation of the Δ^5 double bond; saponification of the 3β-ester; tosylate formation at C-3; and the elimination of *p*-TsOH with potassium acetate in acetic acid. Each compond in the sequence had physical and spectral properties which were in complete accord with literature precedents.[5,7] The anomalous behavior described[1] in 1963 was accurate.

The availability of the mass spectra of six different 5α-androstane-7,17-diones revealed, however, that the true anomaly was *not* in the fragmentation which was not observed but in the remarkable reaction which does occur and which totally dominates the spectra of this series of related compounds. Each spectrum has as its most intense fragment peak a signal at M – 47. The 3β-acetate does not have the expected M – 60 for the loss of acetic acid.[8] The 3β-alcohol does not have a significant peak at M – 18 for the loss of water.[9] The tosylate has a peak at M – 47 as well as at M – (47 + *p*-TsOH).[9] The alkene,[9] the 3,7,17-triketone,[10] and the unsubstituted A-ring compound[11] each show a base peak at M – 47. Similar compounds of the 7-one,[12] 17-one,[13] and 6,17-dione[10] series do not show the M – 47 peak but give more rational fragmentation patterns.

M – 47 must be the loss of one carbon, three hydrogens, and two oxygens. High-resolution mass measurements[14] on the unsubstituted A-ring compound verify this fact. Literature sources[8,10] indicate that these components may be lost as a single entity since metastable ions are noted which correspond to the expected "mother → daughter" transition. This is in keeping with the thought that a two-step process involving multiple bond fissions to the same carbon (for example, loss of water followed by loss of HCO, or vice versa) would not dominate these spectra to the extent that it totally suppresses other well-known facile reactions (loss of acetic acid, loss of water, loss of butadiene). While the earlier workers[8,10] noted that the loss of 47 mass units was characteristic of the 7,17-dione system, they did not refer to the evidence from the metastable ions which they recorded nor did they note the overwhelming influence of this fragmentation process.

5α-Cholest-2-en-7-one was also prepared[15] and while its spectrum is dominated by D-ring cleavages, one can observe the results of the retro-Diels–Alder reaction (M – 54).

A preliminary deuterium-labeling experiment gave a sample of 3β-hydroxy-5α-androstane-7,17-dione, which is 50% d_5 (6,6,8β,16,16), 34% d_4 (6,6,16,16), 12% d_3, and 4% d_2.[12] For this sample, it appears that the major fragmentation was loss of CHD_2O_2 (M – 49). Our work to understand this unprecedented fragmentation process and its specificity continues.

Acknowledgment. We thank the University Research Council of the University of West Florida for a grant.

Registry No. 1, 567-73-7; 3-β-hydroxyandrost-5-en-17-one, 53-43-0.

---

(5) Joska, J.; Fajkoš, J.; Šorm, F. *Collect. Czech Chem. Commun.* **1961**, *26*, 1646.

(6) Salmond, W. G.; Barta, M. A.; Havens, J. L. *J. Org. Chem.* **1978**, *43*, 2057.

(7) (a) Kagan, H. B.; Jacques, J. *Bull. Soc. Chim. Fr.* **1960**, 1551. (b) The positions of the angular methyl groups in the proton NMR were as predicted (Zürcher, R. F. *Helv Chim. Acta* **1963**, *46*, 2054).

(8) Jovanović, J.; Spiteller-Friedmann, M.; Spiteller, G. *Justus Liebigs Ann. Chem.* **1974**, 693.

(9) We thank Mr. J. Moore of the Environmental Protection Agency (Gulf Breeze, FL), Dr. H. Ensley of Tulane University, and Dr. D. Lightner of the University of Nevada, Reno, for assistance in obtaining many of the mass spectra.

(10) Obermann, H.; Spiteller-Friedmann, M.; Spiteller, G. *Chem. Ber.* **1970**, *103*, 1497.

(11) Buchanan, B. G.; Smith, D. H.; White, D. C.; Gritter, R. J.; Feigenbaum, E. A.; Lederberg, J.; Djerassi, C. *J. Am. Chem. Soc.* **1976**, *98*, 6168. The computer program described therein does not predict the appearance of this M – 47 peak.

(12) Beugelmans, R.; Shapiro, R. H.; Durham, L. J.; Williams, D. H.; Budzikiewicz, H.; Djerassi, C. *J. Am. Chem. Soc.* **1964**, *86*, 2832.

(13) Tökés, L.; LaLonde, R. T.; Djerassi, C. *J. Org. Chem.* **1967**, *32*, 1012.

(14) Personal communication from Dr. D. H. Smith, Stanford University.

(15) Hodge, P.; Khan, M. N. *J. Chem. Soc., Perkin Trans. 1* **1975**, 809. The melting point of our compound agreed with that reported in this paper and not with that of Davies and Summers.[16]

(16) Davies, A. R.; Summers, G. H. R. *J. Chem. Soc. C* **1967**, 1227.

Jerome E. Gurst,* Alan K. Schrock
Department of Chemistry
University of West Florida
Pensacola, Florida 32504

Received May 30, 1980

3-(Phenylseleno)-2-propenal as a Versatile Unit for Oxetane Ring Formation

Summary: Treatment of 1-alkyl-3-(phenylseleno)-2-propen-1-ol with 2 equiv of MCPBA followed by sodium hydroxide in aqueous methanol gave 2-alkyl-3-methoxyoxetane in good yield.

Sir: Oxetane ring formation has received extensive attention especially in connection with the synthesis of thromboxane A_2 derivatives.[1] For the preparation of oxetanes, photochemical reaction of olefins with carbonyl compounds (Paterno–Büchi reaction)[2] and ring closure of 1,3-diol derivatives[3] have been widely employed. Recently sodium *S*,*S*-dimethyl-*N*-(*p*-toluenesulfonyl)sulfoximine has also been used as a convenient reagent for the conversion of carbonyl compounds to oxetanes via their oxirane derivatives.[4]

We have been interested in the novel reactivity[5] of phenyl vinyl selenoxides and have described their unique cyclopropanylation reaction with ketone enolates.[6] Fur-

---

(1) See, for example: Mitra, A. "The Synthesis of Prostaglandins"; John Wiley and Sons: New York, 1977; pp 303–320.

(2) Büchi, G; Kofron, J. T.; Koller, E; Rosenthal, D. *J. Am. Chem. Soc.* **1956**, *78*, 876. Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301. Coyle, J. D.; Carless, H. A. J. *Chem. Soc. Rev.* **1972**, *1*, 465 and references cited therein.

(3) Noller, C. R. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 835. Henbest, H. B.; Millard, B. B. *J. Chem. Soc.* **1960**, 3575 Rosowsky, A.; Tarbell, D. S. *J. Org. Chem.* **1961**, *26*, 2255. Wojtowicz, J. A.; Polak, R. J.; Zaslowsky, J. A. *Ibid.* **1971**, *36*, 2232. Richardson, W. H.; Golono, C. M.; Wachs, R. H.; Yelvington, M. B. *Ibid* **1971**, *36*, 943. Hudrlick, P. F.; Hudrlick, A. M.; Wan, C.-N. *Ibid.* **1975**, *40*, 1116. Kitagawa, Y; Itoh, A.; Hashimoto, S.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 3864.

(4) Welch, S. C.; Prakasa Rao, A. S. C. *J. Am. Chem. Soc.* **1979**, *101*, 6135, and for reactions using oxetanes, see references cited therein.

(5) Some of the reactions using vinyl selenoxides were reported: Sevrin, M.; Dumont, W.; Krief, A. *Tetrahedron Lett.* **1977**, 3835.

(6) Shimizu, M.; Kuwajima, I. *J. Org. Chem.* **1980**, *45*, 2921.

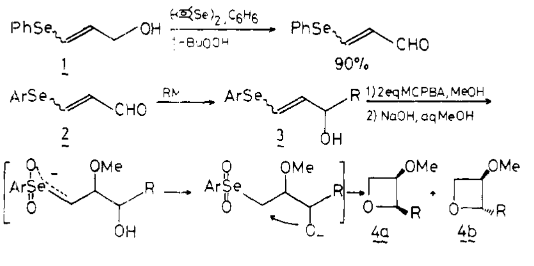
Table I. Preparation of 3-Methoxyoxetanes 4[a]

entry	Ar	olefin geometry	R-M	% yield of 4[b]
1	C_6H_5	*E*	$C_6H_5CH_2CH_2MgCl$	80
2	C_6H_5	*Z*	$C_6H_5CH_2CH_2MgCl$	78
3	p-ClC_6H_4	*Z*	$C_6H_5CH_2CH_2MgCl$	69
4	C_6H_5	*E*	$C_{10}H_{21}MgBr$	78
5	C_6H_5	*Z*	$C_{10}H_{21}MgBr$	72
6	C_6H_5	*Z*	$C_6H_{13}MgBr$	66
7	p-ClC_6H_4	*Z*	C_6H_5MgBr	66
8	C_6H_5	*E*	C_6H_5Li	80
9	C_6H_5	*E*	$C_5H_{11}CHLiCO_2C(CH_3)_3$	81

[a] Reactions were carried out on 0.5-mmol scale as described in the text. [b] Isolated overall yield from 2. All compounds gave satisfactory spectral and analytical data.

ther examinations into the utility of vinyl selenoxides and/or their selenone analogues as conjugate addition acceptors led to a new finding that 3-(phenylseleno)-2-propenal serves as a versatile building unit for the synthesis of oxetane rings. This paper describes its utility as a convenient precursor of 3-methoxyoxetanes.

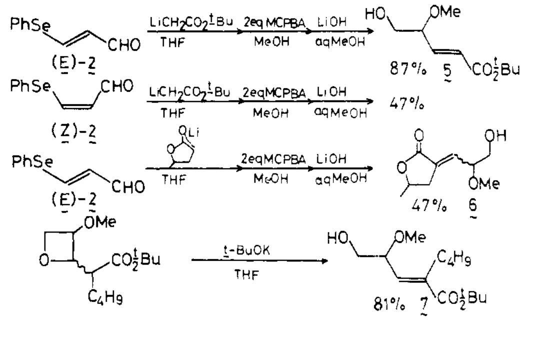
3-(Phenylseleno)-2-propenal serves as an efficient acceptor of nucleophiles such as Grignard reagents, alkyllithiums, and ester or lactone enolates to give allylic alcohols in excellent yields without affecting the phenylseleno moiety. 3-(Phenylseleno)-2-propenal was easily prepared in excellent yield by oxidation[7] of the corresponding alcohol[8] with dimesityl diselenide and *tert*-butyl hydroperoxide as reported previously. On treatment with 2 equiv of MCPBA followed by sodium hydroxide in aqueous methanol, the 1-alkyl-3-(phenylseleno)-2-propen-1-ols gave the corresponding 2-alkyl-3-methoxyoxetanes in good yields. The syntheses of various 3-methoxyoxetanes are summarized in Table I. (*E*)-3-(Phenylseleno)-2-propenal usually gave better results than its *Z* isomer,[9] and 3-methoxyoxetanes were prepared in high overall yields from 2.



In the cyclopropanylation reaction[6] reported previously, electron-withdrawing substituents on the aryl selenide facilitated the reaction. In this oxetane formation, however, *p*-chlorophenyl derivatives (entries 3 and 7) did not serve as better conjugate addition acceptors than its phenyl analogues. The use of water and ca. 2 equiv of MCPBA resulted in higher yields. The former appears to prevent contamination with unidentified byproducts[10] and the latter converts the selenides to selenones.[11]

Close examination of the reaction reveals that both (*E*)-3-(phenylseleno)-2-propenal and its *Z* isomer usually gave *cis*-oxetane (**4a**) predominantly. For example, in the preparation of 3-methoxy-2-(2-phenylethyl)oxetane (entries 1 and 2), a 66:34 ratio of cis (**4a**) vs. trans (**4b**) isomers for entry 1 and a 69:31 ratio for entry 2 were obtained.[12] A similar ratio (ca. 2:1 cis–trans) was obtained in every case in Table I.

When *tert*-butyl acetate[13] or γ-valerolactone enolate was employed as the initial nucleophile, a facile ring opening of the oxetane ring of the intermediate product took place to give **5** or **6** directly from **2** in good overall yield. In this case, the *E* isomer proved far superior to its *Z* isomer. On the other hand, *tert*-butyl hexanoate gave the desired oxetane in good yield. This compound was stable under the reaction conditions employed above, and the ring opening was performed under more forcing conditions, e.g., treatment with potassium *tert*-butoxide in THF.



In the case with γ-valerolactone, the oxetane was obtained as the crude product by using lithium hydroxide in place of sodium hydroxide in methanol. However, this compound underwent ring opening during attempted pu-

---

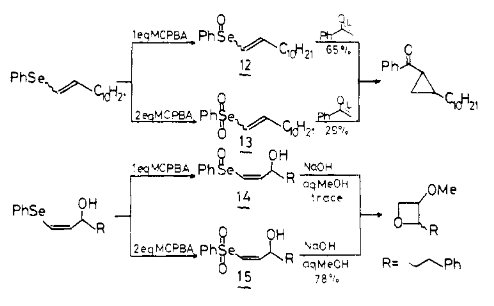
[7] Shimizu, M.; Kuwajima, I. *Tetrahedron* Lett. **1979**, 2801. Shimizu, M.; Urabe, H.; Kuwajima, I. *Angew. Chem.*, submitted for publication.

[8] Prepared by treatment of 3-(phenylseleno)-1-propene oxide with sodium hydride in THF.

[9] Separation of the *E* isomer from the *Z* isomer was readily performed by silica gel column chromatography.

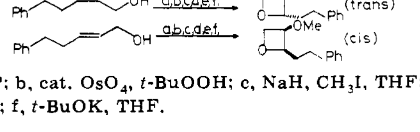
[10] In the absence of water, a decrease in the product yield was observed. This observation suggests that a hydrated selenium species may in part work as leaving group in the present reaction.

[11] We have examined several systems for the formation of phenyl vinyl selenones. It has already been reported that treatment of phenyl vinyl selenide with 1 equiv of MCPBA produced the corresponding phenyl vinyl selenoxide.[5] On the other hand, on treatment with 2 equiv of MCPBA, phenyl vinyl selenide gave a colorless oil which was assigned as phenyl vinyl selenone by spectroscopic and elemental analyses. The difference in the reactivity between vinyl selenoxide and selenone is shown in the following equations:



In the cyclopropanylation reaction,[6] vinyl selenoxide works more effectively than vinyl selenone. In contrast, the present reaction proceeded only with vinyl selenone. The intermediate vinyl selenone **15** was also assigned by spectroscopic and elemental analyses.

[12] The isomeric ratios were determined by GLC analyses (column PEG-20M on Diasolid L, 2 m), using authentic samples prepard in the following manner:



a, H^+, DHP; b, cat. OsO_4, *t*-BuOOH; c, NaH, CH_3I, THF; d, H^+; e, *p*-TsCl, Py; f, *t*-BuOK, THF.

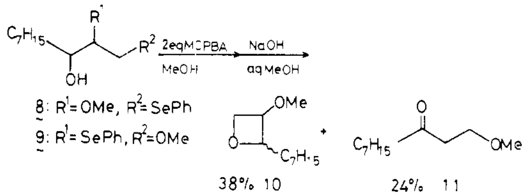
We assume that this oxetane forming reaction proceeds under equilibrium conditions. Detailed explanation of the stereochemistry of this reaction will appear in a full paper.

[13] Rathke, M. W.; Sullivan, D. F. *J. Am. Chem. Soc.* **1973**, *95*, 3050.

J. Org. Chem. **1980**, *45*, 4065–4067 **4065**

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.

Makoto Shimizu, Isao Kuwajima*
Department of Chemistry
Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152, Japan

Received May 27, 1980

---

[14] Liotta, D.; Santiesteban, H. *Tetrahedron Lett.* 1977, 4369.

[15] Nicolaou, K. C.; Claremon, D. A.; Barnett, W. E.; Seits, S. P. *J. Am. Chem. Soc.* **1979**, *101*, 3704 and references cited therein.

[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.

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

---

[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).

[8] A. Padwa, S. Nahm, and E. Sato, *J. Org. Chem.*, **43**, 1664 (1978); A. Padwa and S. Nahm, *J. Org. Chem.*, **44**, 4746 (1979).

[9] P. Caramella and K. N. Houk, *J. Am. Chem. Soc.*, **98**, 6397 (1976); P. Caramella, R. Gandour, J. A. Hall, C. G. Deville, and K. N. Houk, *J. Am. Chem. Soc.*, **99**, 385 (1977).

[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).

0022-3263/80/1945-4065$01.00/0 © 1980 American Chemical Society