(Alkylthio)- and (phenylthio)methoxycarbenes from oxadiazolines

Hui-Teng Er, David L. Pole, and John Warkentin

Abstract: Four 2-methoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazolines bearing an alkylthio or arylthio group at C2 were prepared. The oxadiazolines undergo thermolysis at 60–80°C in solution to afford the corresponding oxythiocarbene intermediates. In the absence of carbene traps, dimers of the carbenes were formed. The carbenes were trapped with ethyl crotonate, with dichloromaleic anhydride, with dimethyl acetylenedicarboxylate, and with phenyl isocyanate. Phenyl isocyanate traps methoxy(methylthio)carbene to form two types of adducts, both fundamentally different from the product obtained from reaction of dimethoxycarbene with phenyl isocyanate. All of the adducts have structures consistent with nucleophilic behaviour of the carbenes.

Key words: oxythiocarbene, oxadiazoline, thermolysis, nucleophilic.

Résumé : On a préparé quatre 2-méthoxy-5,5-diméthyl-Δ^3-1,3,4-oxadiazolines portant un groupe alkylthio ou arylthio en C2. Les oxadiazolines subissent une thermolyse vers 60 à 80°C, en solution, pour conduire aux oxythiocarbènes intermédiaires correspondants. En présence de pièges à carbène, il y a formation des dimères des carbènes. Les carbènes peuvent être piégés par le crotonate d'éthyle, l'anhydride dichloromaléique, l'acétylènedicarboxylate de diméthyle et l'isocyanate de phényle. L'isocyanate de phényle piège le méthoxy(méthylthio)carbène pour former deux nouveaux types d'adduits qui sont tous deux fondamentalement différents du produit obtenu par réaction du diméthoxycarbène avec l'isocyanate de phényle. Tous les adduits ont des structures qui sont en accord avec le comportement nucléophile des carbènes.

Mots clés : oxythiocarbène, oxadiazoline, thermolyse, nucléophile.

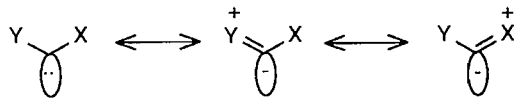
[Traduit par la rédaction]

Introduction

Singlet carbenes bearing donor substituents can have ambiphilic or nucleophilic properties (1). These properties result from conjugative donation of electron density into the formally vacant *p*-orbital of the singlet, Scheme 1. The importance of the dipolar contributor is a factor that determines the philicity of the carbene carbon. Dimethoxycarbene, for example, attacks phenyl isocyanate (2) as depicted in Scheme 2, and it reacts with maleic anhydrides (3) as shown in Scheme 3. The products are readily accounted for in terms of initial carbonyl addition to form a dipolar intermediate.

The availability of the exchange method (Scheme 4) for synthesis of various dioxy oxadiazolines from 2-acetoxy-2-methoxy-Δ^3-1,3,4-oxadiazolines (**1**) (4) suggested that it might be possible to prepare 2-alkylthio- and 2-arylthio-2-methoxy-Δ^3-1,3,4-oxadiazoline analogues of **2**, Scheme 4. Their thermolysis would be expected to take the cycloreversion – ylide fragmentation sequence that 2,2-dialkoxy oxadiazolines appear to follow (2*a*, 3–5), leading to (alkylthio)methoxycarbene analogues of **3***a* and corresponding

Scheme 1.



(arylthio)methoxycarbene analogues of **3***b*, Scheme 4, for convenient study of their chemical reactions. Such carbenes have not been reported, to the best of our knowledge.

Methods, results, and discussion

2-Acetoxy-2-methoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline (**1**) containing ca. 30% of acyclic by-product **4** was prepared by oxidation of the methoxycarbonyl hydrazone of acetone with Pb^{IV} acetate in CH_2Cl_2 as previously described (4), Scheme 5.

Treatment of the mixture of **1** and **4** with the appropriate thiol (Scheme 6) afforded **5** contaminated with **4**. Destruction of **4** with aqueous base and chromatography of the residue afforded pure **5** in yields ranging from 44 to 80% for the exchange step of Scheme 6. Their spectroscopic properties are given in the experimental section.

Thermolysis of compounds **5***a–c* in benzene was followed by ^1H NMR spectroscopy. Disappearance of **5** was first order in each case and the first-order rate constants were the same within experimental error: $k(60°C) = 2.07(\pm 0.09) \times 10^{-5}\ s^{-1}$. While the effect of the sulfur-bound group (R) at C2 on the thermolysis rate constant is very small, the sulfur atom itself has a significant rate-enhancing effect, for 2,2-dimethoxy-5,5-

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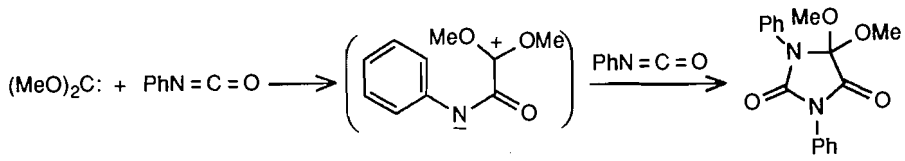
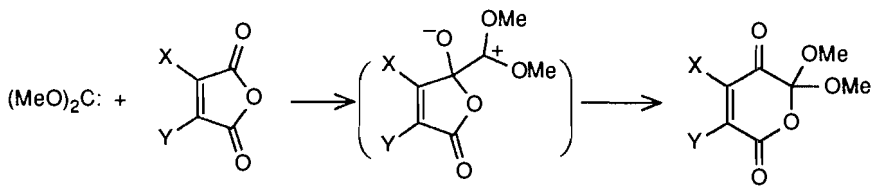
Scheme 2.

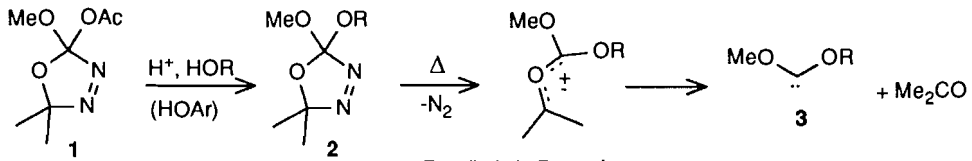


Scheme 3.



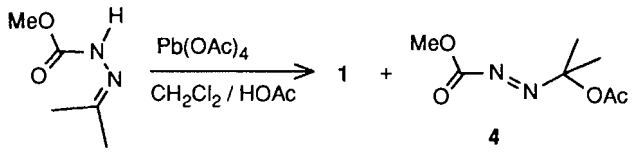
X,Y= H, Me, Cl, Br, for example, in various combinations

Scheme 4.

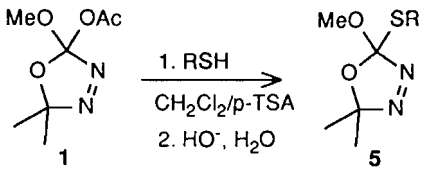


a: R= alkyl *b*: R= aryl

Scheme 5.



Scheme 6.



a: R= Ph, *b*: R= CH_2Ph, *c*: R= Et, *d*: R= Me

dimethyl-Δ^3-1,3,4-oxadiazoline undergoes thermal cycloreversion with a comparable rate constant at a temperature 40° higher, i.e., 100°C (2*a*). One potential source of the rate enhancement by a thio substituent is the polarizability of sulfur. Most likely, negative charge develops at positions 2 and 5 of the oxadiazoline as the ylide-like transition state (**6**) develops. Sulfur substitutents exert an anion-stabilizing role, as in anion equivalents generated from 1,3-dithiane. A second source of the rate enhancement could be a ground state energy difference between thio and oxy analogues. The 2,2-dimethoxy oxadiazoline has four electronegative moieties attached to C2, compared to three plus a sulfur-bound group for **5***a*–**5***c*. Clumping electronegative groups on the same carbon atom has the surprising effect of increasing thermodynamic stability (6).

Thermolysis of **5** in benzene afforded the corresponding carbene dimers **7** and **8** (Scheme 7), in yields ranging from 55 to 65%. The *E*:*Z* ratios ranged from 1.2 to 1.8, Table 1.

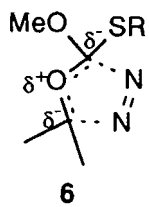


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Table 1. Yields and isomer ratios.

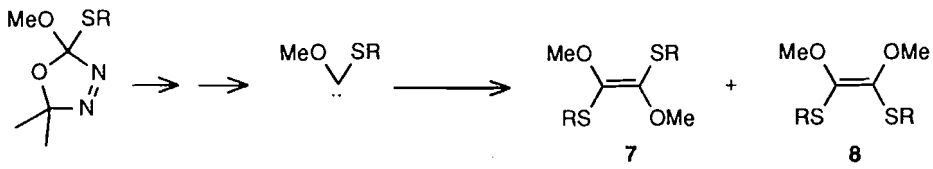
Oxadiazoline	Thermolysis product		*E* : *Z*
5*a*: R = Ph	**7***a*: 35%	**8***a*: 20%	1.8
b: R = CH_2Ph	*b*: 32%	*b*: 27%	1.2
c: R = Et	*c*: 38%	*c*: 27%	1.4
d: R = Me	*d*: 32%	*d*: 27%	1.2

Preliminary assignment was based on the observation that the major product was eluted first during chromatography and that it ought to be the *E* isomer, in which all dipole vectors should cancel. That assignment was subsequently confirmed by means of the single crystal X-ray structure of **7***b*.[2] The fact that carbene dimers and acetone were major products suggests that all four oxadiazolines (**5**) fragment thermally to form N_2 and a carbonyl ylide, and that the latter fragments efficiently to afford the appropriate carbene and acetone (Scheme 7). A competitive 1,3-dipolar cycloreversion of **5***a* afforded methyl phenylthio carbonate (**9**) and, presumably, 2-diazopropane, Scheme 8.

In the ^{13}C NMR spectra of the carbene dimers, the vinyl

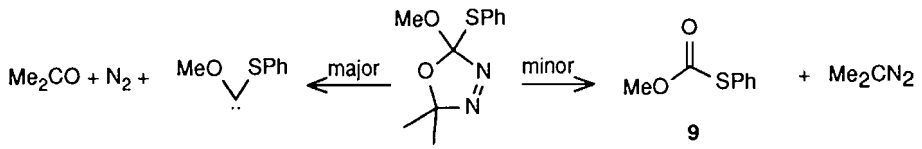
[2] Publication of the crystal and molecular structures will be delayed in the expectation that the data could be made more meaningful by inclusion of the structure of a *Z* isomer.

Scheme 7.

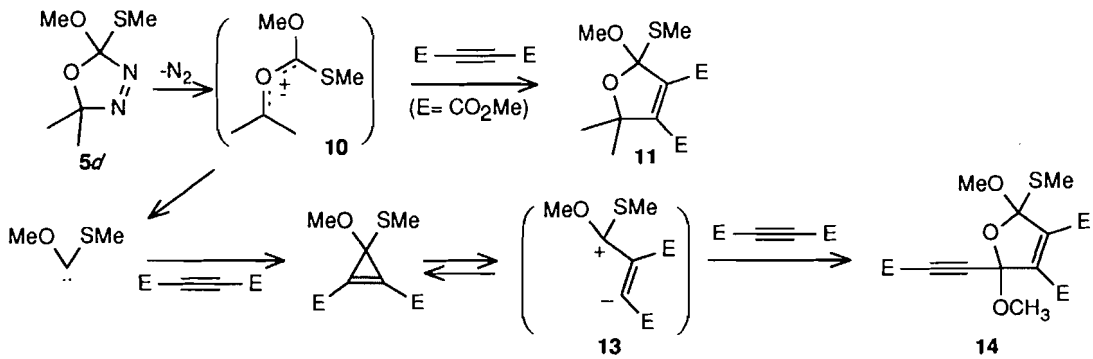


a: R= Ph, *b*: R=CH_2Ph, *c*: R= Et, *d*: R=Me

Scheme 8.



Scheme 9.



carbon signals are near δ = 143 in **7**(*a–d*) and **8**(*a–d*). For comparison, the vinylic signals of 1,2-dimethoxy-1,2-diphenoxyethenes occur near δ = 138, and those of tetraalkoxyethenes near δ = 141 (7).

Experiments designed to intercept reactive intermediates were revealing. Initial cycloreversion to N_2 and a carbonyl ylide (**10**) was inferred for the case of **5***d* from a reaction with dimethyl acetylenedicarboxylate (DMAD). The reaction mixture was complex, but it was possible to isolate what is formally the ylide–DMAD adduct (**11**), Scheme 9, along with some carbene–DMAD adduct (**14**). This result indicates that a concerted mechanism recently proposed by Smith (8), leading from a 2,2-dialkoxyoxadiazoline analogue of **5** *directly* to carbene, N_2, and acetone, may not be general. However, there is an alternative mechanism for formation of **11**, involving cycloaddition of a carbene–DMAD dipolar adduct to acetone. The fact that the acetone concentration started at zero, and remained below the final DMAD concentration throughout, makes that mechanism less likely. Nevertheless, additional experiments are needed to secure the origin of **11**.

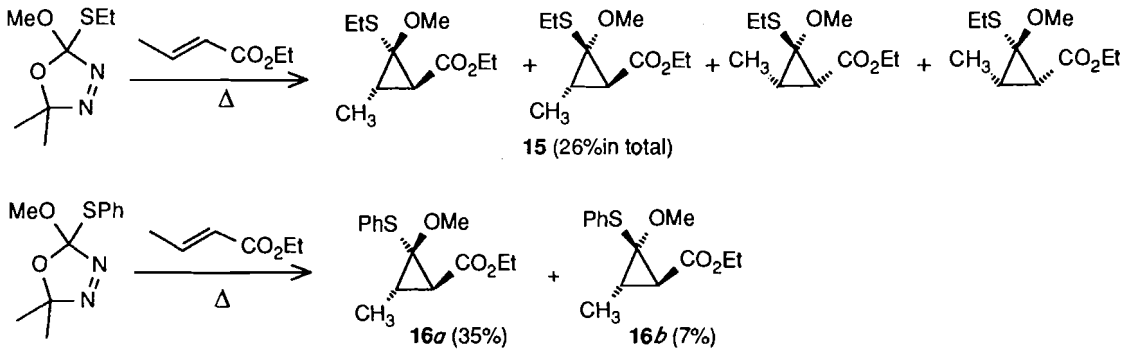
Cycloadducts from an ylide intermediate were not obtained with the other trapping agents, ethyl crotonate, dichloromaleic anhydride, or phenyl isocyanate. Possibly the fragmentation of the ylide to carbene and acetone is fast and only very reactive dipolarophiles can compete at relatively low concentrations (ca. 0.1 M). The overall 1:2 stoichiometry leading to **14** (Scheme 9) for reaction of (methoxy)methylthiocarbene with DMAD has been reported for the case of dimethoxycarbene by Hoffmann et al. (9). A dipolar adduct similar to **13**, with vinyl carbene character, was proposed (9), Scheme 9. The reason for addition to a carbonyl group of DMAD in the second step, rather than to the triple bond, is not well understood. Steric hindrance may be responsible, in part.

Ethyl crotonate intercepted carbene intermediates although not their carbonyl ylide precursors. Thus, thermolysis of **5***a* in the presence of ethyl crotonate afforded four diastereomeric ethyl cyclopropanecarboxylates (**15**), Scheme 10, in 26% total yield. The diastereomers could not be separated but the relative yields (1:2:1.6:3.2) could be obtained from the ^{1}H NMR spectrum of the mixture by integration of the four methoxy signals. The EI and the CI mass spectra gave the appropriate $[M]^+$ and $[M + H]^+$ signals. Both carbene dimers (**7***c*, **8***c*) were detectable as minor coproducts, indicating that reaction of (ethylthio)methoxycarbene with ethyl crotonate is relatively slow. Formation of all four diastereomers of **15** is in keeping with a stepwise mechanism of cyclopropanation, as proposed by Hoffmann (9) to account for the observation that dimethoxycarbene reacts with diethyl maleate to afford only the *trans* product of cyclopropanation.

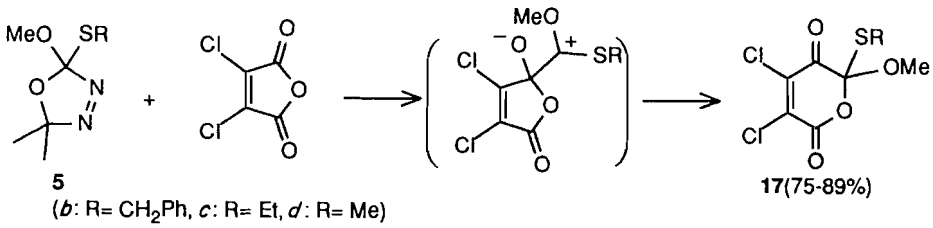
Thermolysis of **5***a* in dry benzene containing ethyl crotonate gave two diasteromeric cyclopropanes (**16***a*, **16***b*) in yields of 35 and 7%. Again, separation of those diastereomers was not achieved and the spectra of the individual isomers were gleaned from the spectra of the mixture. Assignment of structure **16***a* to the major diastereomer is tentative (Scheme 10).

An important feature that determines the different outcomes of trapping with DMAD and trapping with ethyl crotonate is

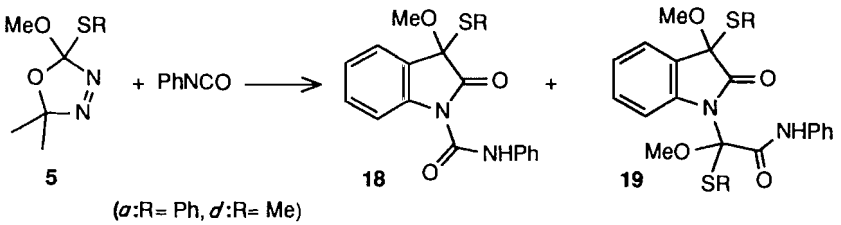
Scheme 10.



Scheme 11.



Scheme 12.



the thermal instability of cyclopropenes. Thus, whereas both reactions presumably result initially in formation of a three-membered ring, cyclopropenes with ester groups at C1 and C2 are thermally labile (10), Scheme 9, whereas cyclopropanes are relatively robust. The former therefore undergo eventual irreversible reaction through a dipolar intermediate (Scheme 9), to afford 1:2 adducts.

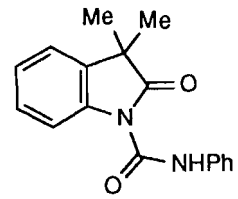
Reactions of the carbenes with dichloromaleic anhydride do not mimick the ones with ethyl crotonate. Overall insertion into the ring C—O bond occurs, presumably by nucleophilic addition to carbonyl carbon (3) followed by 1,2-acyloxy migration, Scheme 11. The structure of **17***d* was secured by means of single crystal X-ray diffraction.[3] Possible reasons for the failure of ethyl crotonate to undergo analogous attack include the lower reactivity of esters compared to anhydrides and a slower follow-up step that might not compete well with reversal.

Thermolysis of **5***a* and of **5***d* in benzene containing excess phenyl isocyanate afforded three products in each case. Centrifugal chromatography led to ready separation of a rapidly eluting minor product identified as 2:1 adduct **18***a* from **5***a*, and **18***d* from **5***d*, Scheme 12. *N*-Phenylcarbamoyl oxindoles such as **18** are readily recognized, having NH absorption and an intense broad carbonyl band in the infrared spectrum. The ^{1}H NMR spectrum included, in each case, a low-field doublet ($\delta \simeq 8.3, J \simeq 8$ Hz) corresponding to the oxindolyl aryl hydrogen nearest to the phenylcarbamoyl group. *N*-Acyl indoles also have an especially deshielded aryl hydrogen for the same reason: the proximity of the amide carbonyl oxygen to an aryl hydrogen separated from it by five bonds (11). An analogous product (**20**) had already been observed, from reaction of 2-diazopropane with phenyl isocyanate (12). The fact that the 2:1 adduct was a minor product was surprising, Hoffmann's group (2*b*) having identified *only* a 2:1 adduct from reaction of dimethoxycarbene with phenyl isocyanate. Also surprising was the fact that Hoffmann's product was apparently a hydantoin (Scheme 2) whereas ours, from methoxy(methylthio)carbene, was clearly an oxindole. Thermolysis of 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline in benzene containing phenyl isocyanate afforded the Hoffmann hydantoin (65% yield), confirming that dimethoxycarbene and methoxy(methylthio)carbene, each generated thermally from an oxadiazoline precursor, afford quite different 2:1 adducts with phenyl isocyanate.

Equally surprising was the finding that the major products from thermolysis of **5***d* (or **5***a*) in the presence of phenyl isocyanate were 2:2 adducts (**19**) obtained as mixtures of diastereomers. In the case of **19***a* the diastereomers were separable by chromatography but **19***b* could not be separated. Attempts to grow a single crystal from either diastereomer of **19***a*, for single crystal X-ray diffraction, were not successful.

[3] Publication of the details will be delayed in the expectation that an analogous structure, from either a bis(alkylthio)carbene or an alkoxyaminocarbene, will become available for comparisons.

The spectra fit the oxindole structure (**19**) well, for diastereomeric products would be expected in each case, **19***a*, **19***d*. In both cases, the ^{13}C NMR spectra and the IR spectra suggested carbonyl groups in different environments. Those features rule out the 1,4-piperazine-2,5-diones (**21**) and their isomers **22**. The ring carbonyl group and the other amide carbonyl group are in quite different environments and the ^1H NMR spectra rule out the isomeric **23**. Structures such as **23** should also show the characteristic low-field doublet (ca. 8.3 ppm, *J* ca. 8 Hz) of carbamoyl oxindoles, outlined above. Moreover, compounds **19** showed a broad singlet (δ = 7.6 and 8.3 for **19***a* and **19***d*, respectively) in the ^1H NMR spectra, as expected for NH of an amide. Finally, the mass spectra included peaks at *m/z* = 119 and *m/z* = 120, for **19***a* and **19***d*, respectively, attributable to PhNCO and PhNHCO fragments expected from **19**, but not from **23**, as well as the appropriate molecular ions.



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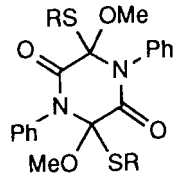

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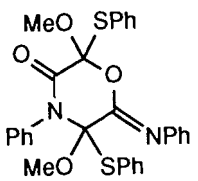

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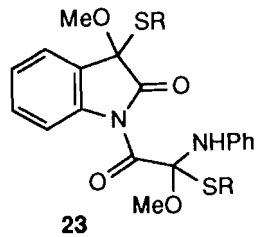

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What structural features and mechanisms might account for the very different behaviours of dimethoxycarbene and methoxy(methylthio)carbene toward phenyl isocyanate? The connectivities of the products suggest a common first step: nucleophilic addition of the carbene to carbonyl carbon of the isocyanate to form a dipolar intermediate, as suggested by Hoffmann et al. (2*b*), Scheme 13. Presumably such an intermediate is equilibrated with the corresponding α-lactam and iminooxirane (not illustrated). We postulate that the dipolar intermediate of Scheme 2 is more stable than its analogue **24**, because the resonance contributors in the cationic portion of the former are equivalent and because the carbonyl double bond is much stronger than the thiocarbonyl double bond. As a consequence, the rate constant for intramolecular ring closure, to form the dialkoxy analogue of **25**, could be small enough to permit it to undergo intermolecular reaction (Scheme 2) with phenyl isocyanate to afford the hydantoin. On the other hand, **24** cyclizes rapidly to **25**, which cannot aromatize to **26** intramolecularly because a concerted 1,3-H shift would have to be antarafacial (13). It can accumulate, therefore, to react with **25** in an acid–base reaction, generating ion pair **27**. Collapse of the latter would generate the observed diastereomeric 2:2 adducts, **19**, Scheme 13. While this explanation is attractively simple, it is not unique and must be regarded as tentative.

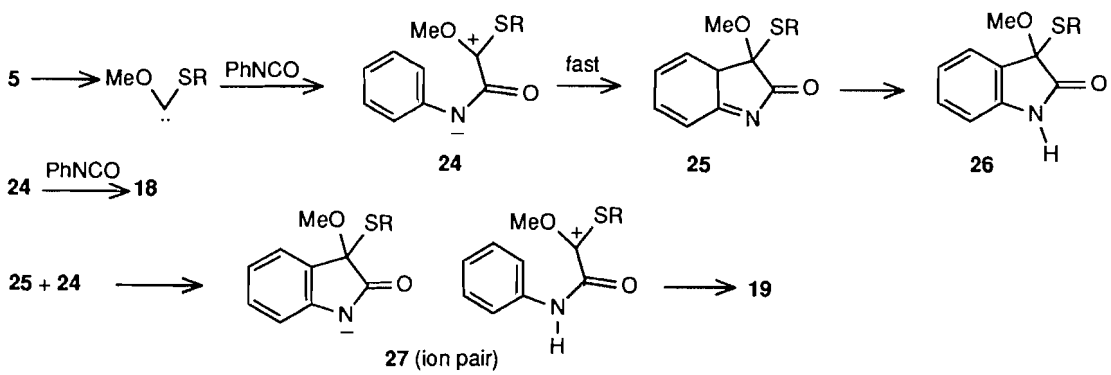
Experimental

^1H NMR spectra were run with $CDCl_3$ or C_6D_6 solutions, with a 200 or a 300 MHz Bruker spectrometer, and ^{13}C spectra were acquired at 50 MHz with a Bruker AC200 spectrometer. Infrared spectra were taken from solutions in CCl_4, in a cell of 0.5 mm path length, with a Biorad FTS-40 spectrophotometer. Solvent absorptions were subtracted. The IR bands are labelled qualitatively with the symbols s and m for strong and medium intensities, respectively. Weaker bands are not labelled and very weak bands are not included. Raman spectra were obtained from neat samples, with a Jobin Yvon/ISA Mole S-3000 spectrometer.

2-Methoxy-5,5-dimethyl-2-phenylthio-Δ^3-1,3,4-oxadiazoline (*5a*)

A solution of *p*-toluenesulfonic acid (pTSA, 0.40 g) in benzene (15 mL) was refluxed for about 1 h in a flask fitted with a Dean and Stark trap containing molecular sieves in the water trapping arm. After the solution had cooled, a solution of 2-acetoxy-2-methoxy-5,5-dimethyl-Δ^3-oxadiazoline (**1**) containing **4** (total weight 5.0 g, 64% **1** by ^1H NMR assay) and thiophenol (2.0 mL) in dichloromethane (10 mL) was added. More dichloromethane (30 mL) was used to rinse traces of thiophenol solution into the flask containing pTSA and the reaction solution so obtained was refluxed under N_2 for 16 h. The solution was cooled, KOH pellets were added, and the heterogeneous mixture was stirred rapidly for 2 h. Water was added and the mixture was shaken vigorously before the organic layer was separated and extracted several times with

Scheme 13.



water. Drying over $MgSO_4$ and evaporation of the solvents left a residue that was chromatographed (Chromatotron, 4 mm plate, hexane) to afford the title compound as a white solid (69%), mp 38–39°C. IR (CCl_4) cm^{-1}: 3064, 2993, 2943, 2895, 2838, 1477, 1441, 1366, 1264, 1238, 1204, 1128s, 1064s, 1025, 976m, 959m, 911, 826, 692, 628, 581, 516, 479. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.14 (s, 3H), 1.50 (s, 3H), 3.52 (s, 3H), 7.28–7.34 (m, 3H), 7.57–7.63 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 22.6, 25.0, 52.2, 122.8 (C5), 128.8, 129.0, 129.2, 135.7, 137.2. MS (EI) *m/z*: 207 ($M^+ - OCH_3$, 5), 153 ($MeOCHSPh^+$, 24), 129 ($M^+ - SPh$, 69), 109 ($C_6H_5S^+$, 100).

2-Benzylthio-2-methoxy-5,5-dimethyl-Δ³-1,3,4-oxadiazoline (*5b*)

The procedure described above was followed. From 15 g of **1** plus **4** (63% **1**), benzyl mercaptan (5.9 mL), pTSA (1.0 g), and CH_2Cl_2 (120 mL) there was obtained, after refluxing overnight, a liquid product that was chromatographed (Chromatotron, 4 mm plate, 5% EtOAc in hexane) to afford 5.58 g (44%) of **5***b* as a clear liquid. IR (CCl_4) cm^{-1}: 3087, 3031, 2992, 2941, 2839, 1731, 1603, 1496, 1457, 1368, 1237, 1203, 1124s, 1069s, 979m, 910, 828, 703m, 625, 583, 465. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.53 (s, 3H), 1.57 (s, 3H), 3.40 (s, 3H), 4.09 (d, $^2J = -12.7$ Hz, 1H), 4.20 (d, $^2J = -12.7$ Hz, 1H), 7.24–7.36 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 23.1, 24.8, 34.8, 51.5, 122.6 (C5), 127.1, 128.4, 128.9, 136.6, 137.1. MS (EI) *m/z*: 221 ($M^+ - OCH_3$, 2), 183 ($M^+ - N_2 - C_3H_5$, 5), 167 ($MeOCHSCH_2Ph^+$, 14), 135 ($PhCH_2CS^+$, 17), 133 ($M^+ - N_2 - PhCH_2$, 37), 129 ($M^+ - SCH_2Ph$, 62), 91 (100), 73 (70). MS (CI, NH_3) *m/z*: 270 ($M^+ + NH_4$).

2-Ethylthio-2-methoxy-5,5-dimethyl-Δ³-1,3,4-oxadiazoline (*5c*)

The exchange method described above was used, with impure oxadiazoline **1** (15.0 g of **1** + **4**, containing 10.5 g, 0.056 mol of **1**), ethanethiol (4.69 mL, 0.062 mol, 97% pure), and pTSA (1.06 g, 5.6 mmol, dried by azeotropic distillation of a benzene solution) in CH_2Cl_2 (120 mL). Heating at reflux for 17 h, cooling, addition of KOH pellets (ca. 2 g), and stirring for several hours caused a change in colour to pale yellow. Addition of water, shaking, separation, and drying of the organic phase and evaporation of the solvent left a residual oil that was chromatographed on silica gel (5% EtOAc in hexane) to afford **5***c* as a clear liquid (6.05 g, 57%). IR (CCl_4) cm^{-1}: 2991, 2938, 2874, 2837, 1456m, 1371, 1268, 1237, 1203m, 1180, 1124s, 1070s, 977m, 910m, 827, 685, 580, 486. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.35 (t, $J = 7.5$ Hz, 3H), 1.54 (s, 3H), 1.57 (s, 3H), 2.81 (dq, $J = 7.5$ and -12.9 Hz, 1H), 2.95 (dq, $J = 7.5$ and -12.9 Hz, 1H), 3.44 (s, 3H). ^1H NMR (200 MHz, C_6D_6) δ: 1.17 (t, $J = 7.4$ Hz, 3H), 1.20 (s, 3H), 1.27 (s, 3H), 2.66 (dq, $J = 7.4$ and -13.0 Hz, 1H), 2.88 (dq, $J = 7.4$ and -13.0 Hz, 1H), 3.20 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 15.2, 23.0, 24.5, 24.7, 51.3, 122.0 (C5), 136.9 (C2). MS (EI) *m/z*: 129 ($M^+ - SEt$, 8), 105 (10), 84 (28). MS (CI, NH_3): 189 ($M^+ - H$).

2-Methoxy-2-methylthio-5,5-dimethyl-Δ³-1,3,4-oxadiazoline (*5d*)

A solution of *p*-toluenesulfonic acid (1.0 g, 0.005 mol) in benzene (30 mL) was refluxed in a Dean and Stark apparatus. The dried portion was added to a solution of **2** (15 g of **1** (63%) containing **4**) in dry CH_2Cl_2 (120 mL). Cold methyl mercaptan, collected in a Dry Ice trap after passage of the gas through a tube packed with anhydrous $MgSO_4$, was added from a syringe. The reaction vessel was sealed and maintained at 45°C overnight in an oil bath. Its contents were then transferred to a 250 mL flask containing ca. 2 g of KOH pellets. Vigorous stirring for a few hours, followed by addition of water, shaking, separation, extraction of the organic phase with water, drying, and removal of the solvent, left a residue that was subjected to column chromatography to afford pure **5***d* as a clear liquid, 7.08 g (80%). IR (CCl_4) cm^{-1}: 2993, 2940, 2893, 1561, 1459, 1437, 1367, 1237, 1203, 1124, 1072s, 999, 980, 910, 827, 702, 682, 626, 581. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.55 (s, 3H) 1.57 (s, 3H), 2.33 (s, 3H), 3.46 (s, 3H). ^1H NMR (200 MHz, C_6D_6) δ: 1.20 (s, 3H), 1.25 (s, 3H), 2.09 (s, 3H), 3.20 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 12.9, 23.2, 24.9, 51.4, 122.6 (C5), 136.6 (C2). MS (EI) *m/z*: 176 (M^+, 1), 145 ($M^+ - OCH_3$, 3), 129 ($M^+ - SCH_3$, 24), 90 (34), 75 (100). MS (CI, NH_3) 177 ($M^+ + H$).

Thermolysis of 2-methoxy-5,5-dimethyl-2-phenylthio-Δ³-1,3,4-oxadiazoline in benzene

A solution of **5***a* (0.209 g, 0.878 mmol) in benzene (10 mL) was refluxed overnight under N_2 in a Dean and Stark apparatus. The residue left after evaporation of the solvent consisted of methyl phenylthio carbonate **9** (0.0103 g, 7%), *E*-1,2-dimethoxy-1,2-di(phenylthio)ethene **7***a* (0.0467 g, 35%), and the corresponding *Z* isomer **7***b* (0.0267 g, 20%), as determined by chromatographic separation (Chromatotron, 1 mm plate).

A similar thermolysis, in which *p*-xylene served as ^1H NMR standard for integration, gave $k(60°C) = 2.04 \times 10^{-5}$ s^{-1} and yields (not isolated) of 8, 48, 40, and 62% for **9**, **7***a*, **7***b*, and acetone, respectively. Methyl phenylthio carbonate was a clear liquid. IR (CCl_4) cm^{-1}: 3066, 3008, 2954, 2888, 2836, 1730s, 1584, 1480, 1435, 1189m, 1143s, 1093, 1025, 689, 673, 556, 532. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.84 (s, 3H), 7.39–7.42 (m, 3H), 7.51–7.55 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 54.5, 127.6, 129.2, 129.6, 134.8, 170.2. MS (EI, GC/MS) *m/z*: 168 (M^+, 38), 137 ($M^+ - OCH_3$, 3), 124 (16), 109 (100), 91 (32), 78 (22), 69 (23), 65 (37). An authentic sample, synthesized by treating methyl chloroformate with thiophenol in the presence of pyridine, had matching spectral characteristics.

E *Dimer of (methoxy)phenylthiocarbene,* 7a

The *E* dimer was a white solid, mp 53–55°C. IR (CCl_4) cm^{-1}: 3065, 3007, 2963, 2932, 2892, 2830, 1796, 1718, 1657, 1583m, 1479m, 1442m, 1265, 1206s, 1146s, 1121, 1081, 1023, 1003, 954, 909, 870, 832, 692s, 520. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.55 (6H), 7.17–7.42 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 58.5, 126.7, 129.0, 129.5, 133.6, 142.8. MS (EI) *m/z*: 304 (M^+, 100), 261 [$(PhS)_2COMe^+$, 91], 218 (32), 195 (13), 153 (28), 109 (PhS^+, 75).

Z *Dimer of (methoxy)phenylthiocarbene,* 8a

Clear liquid. IR (CCl_4) cm^{-1}: 3066, 3004, 2965, 2935, 2894, 2832, 1774, 1725, 1581m, 1479m, 1442, 1264, 1198s, 1122 br, 1085, 1025m, 1006, 959, 880, 692m, 566. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.67 (s, 6H), 7.15–7.36 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 58.6, 126.4, 128.3, 129.1, 134.2, 143.2. MS (EI) *m/z*: 304 (M^+, 100), 261 (90), 195 (14), 109 (75).

Thermolysis of 5*a* in presence of ethyl crotonate

A solution of **5***a* (0.1201 g, 0.504 mmol) and ethyl crotonate (Aldrich, 96%, predominantly *E* isomer, 0.08 mL, 0.60 mmol) in benzene (10 mL) was sealed into a 100 mL glass tube that was then heated in an oil bath (70°C) overnight. The solvent was removed and the residue was chromatographed (Chromatotron, 1 mm plate, washed with Et_3N in hexane, elution with hexane). Five products were isolated: a pair of ethyl cyclopropane carboxylates, **16***a* and **16***b*, **9**, and the carbene dimers **7***a* and **8***a*.

E,Z-*Ethyl 2-methoxy-3-methyl-2-phenylthiocyclopropanecarboxylate (**16**a)*: Major product, 0.0469 g, 35% yield, clear oil. IR (CCl_4) cm^{-1}: 3064, 2981m, 2965m, 2934m, 2903, 2878, 2829, 1735s, 1584, 1480m, 1444m, 1416, 1367, 1318s, 1265m, 1228m, 1201m, 1170 br, 1117m, 1098m, 1049m, 1024, 998m, 911, 864, 692. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.25 (d, J = 6.4 Hz) overlapping δ 1.27 (t, J = 7.1 Hz), sum 6H, 1.83 (d, J = 6.8 Hz, 1H), 2.27 (5 lines, 1H), 3.37 (s, 3H), 4.181 (q, J = 7.1 Hz) overlapping 4.188 (q, J = 7.1 Hz), sum 2H, 7.15–7.28 (m, 3H), 7.44–7.48 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 14.2, 28.9, 36.5, 54.9, 60.9, 78.2, 110.7, 126.1, 128.6, 128.8, 134.7, 168.7. MS (EI) *m/z*: 266 (M^+, 3), 235 ($M^+ - OCH_3$, 18), 220 (100), 205 (25), 193 (85), 157 (89), 129 (45), 109 (50), 69 (47). MS (CI, NH_3) *m/z*: 284 ($M^+ + NH_4$, 74), 267 ($M^+ + H$, 39).

Z,E-*Ethyl 2-methoxy-3-methyl-2-phenylthiocyclopropanecarboxylate (**16**b)*: Minor diastereomer, ca. 7%. This product was obtained as a mixture with **16***a* and only a part of the ^1H NMR spectrum was assignable. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.15 (t, J = 7.1 Hz, 3H), 1.27 (m), 1.87 (d, J = 7.2 Hz, 1H), 2.03 (5 lines, 1H), 3.48 (s, 3H), 4.02 (m, 2H), 7.17–7.58 (m).

Thermolysis of 5*a* in presence of phenyl isocyanate

A solution of **5***a* (0.204 g, 0.858 mmol) and phenyl isocyanate (0.19 mL, 1.7 mmol) in benzene (8 mL) was sealed into a glass tube that was then immersed overnight in an oil bath kept at 70°C. Evaporation of the solvent left a residue that was chromatographed (Chromatotron, 1 mm plate) on SiO_2 with hexane. After the first product (**18***a*) had been eluted the solvent was gradually changed to 5% EtOAc in hexane. Two additional products, diastereomers **19***a*, were eluted slowly. Yields of isolated materials were 10, 39, and 28%, respectively.

*3-Methoxy-1-phenylcarbamoyl-3-phenylthio-oxindole, (**18**a)*: White solid, 0.0335 g, mp 139–140°C, 10%. IR (CCl_4) cm^{-1}: 3260, 3064, 2948, 2891, 2832, 1748s, 1600m, 1552s, 1503, 1470m, 1448, 1340, 1310, 1277, 1243, 1204, 1163m, 1112, 1088, 1022, 970, 913, 693m, 574, 505. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.56 (s, 3H), 7.03–7.15 (m, 3H), 7.33–7.58 (m, 9H), 8.32 (d, J = 8.3 Hz, 1H), 10.36 (s, br, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 53.8, 87.9, 116.8, 120.7, 124.2, 124.5, 124.7, 124.8, 128.8, 129.1, 130.0, 130.9, 136.6, 136.8, 138.5, 149.0, 173.6. MS (EI) *m/z*: 314 (3), 281 (15), 162 (100), 119 (52), 91 (18). MS (CI, NH_3) *m/z*: 391 ($M^+ + H$).

*Major diastereomer of oxindole **19**a*: White solid, mp 169–171°C, 39% (isolated). IR (CCl_4) cm^{-1}: 3411, 3362, 3063, 3034, 2962, 2943, 2891, 2833, 1746s, 1718m, 1604m, 1527s, 1468, 1442m, 1336, 1311, 1279, 1243, 1183, 1158, 1086 br, 1075m, 986, 909s, 692m, 660, 503. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.52 (s, 3H), 3.58 (s, 3H), 6.86–7.54 (m, 20H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 51.2, 54.2, 87.7, 99.0, 111.7, 119.6, 119.9, 123.5, 124.6, 124.8, 125.1, 128.6, 128.7, 128.8, 129.0, 129.6, 129.9, 130.3, 136.1, 136.8, 137.4, 139.7, 162.2, 172.2. MS (EI) *m/z*: 447 (18), 433 (26), 405 (55), 272 (13), 162 (100), 146 (37), 120 (65), 110 (81), 109 (67), 77 (40). MS (CI, NH_3) *m/z*: 560 ($M^+ + NH_4$).

*Minor diastereomer of oxindole **19**a*: White solid, mp 171–173°C, 28% (isolated). IR (CCl_4) cm^{-1}: 3413, 3396, 3061, 2961, 2891, 2830, 1744s, 1719m, 1604m, 1525s, 1468, 1442m, 1337, 1312m, 1281, 1243, 1193, 1117, 1087, 1087, 1066 br, 986, 947, 909, 824, 691m, 504. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.62 (s, 3H), 3.68 (s, 3H), 6.80 (m), 7.01–7.38 (m, 13H), 7.51–7.55 (m, 4H), 7.62 (s, br, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 51.4, 53.6, 87.7, 99.6, 112.1, 119.6, 123.2, 124.2, 124.6, 125.0, 128.5, 128.7, 128.8, 129.0, 129.4, 129.6, 129.8, 130.0, 136.4, 137.0, 137.3, 139.5, 161.9, 171.9. MS (EI) *m/z* (rel. intensity): 433 ($M^+ - SPh$, 22), 405 (34), 272 (13), 162 (100), 110 (26), 109 (31), 77 (32). MS (CI, NH_3) *m/z*: 560 ($M^+ + NH_4$).

Thermolysis of 2-benzylthio-2-methoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline in benzene

A solution of **5***b* (0.1553 g, 0.615 mmol) in benzene (10 mL) was refluxed overnight under N_2 in a Dean and Stark apparatus. The final solution contained acetone and the *E* and *Z* isomers of 1,2-bis(benzylthio)-1,2-dimethoxyethene. Chromatography of the latter (Chromatotron, 1 mm plate, hexane) afforded the *E* isomer **7***b* followed by the *Z* isomer **8***b*. The ratio *E*:*Z* ranged from 1.38 to 1.19 from three runs.

E-*1,2-Bis(benzylthio)-1,2-dimethoxyethene (**7**b)*: White solid, mp 82–84°C, 0.0205 g, 32% yield. IR (CCl_4) cm^{-1}: 3086, 3064, 3031, 3003, 2962, 2933, 2894, 2827, 1716, 1601, 1496, 1454, 1427, 1263, 1238, 1203s, 1136s, 1112, 1071, 954m, 915, 871, 700, 672, 561, 472. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.21 (s, 6H), 3.75 (s, 4H), 7.15–7.30 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 35.9, 57.9, 126.9, 128.3, 128.8, 138.6, 143.5. MS (EI) *m/z*: 332 (M^+, 4), 241 ($M^+ - CH_2Ph$, 45), 91 ($PhCH_2^+$, 100). MS (CI, NH_3) *m/z*: 333 ($M^+ + H$).

Z-*1,2-Bis(benzylthio)-1,2-dimethoxyethene (**8**b)*: Yellow oil, 0.0173 g, 27% yield. ^1H NMR (200 MHz, $CDCl_3$) δ: 3.54 (s, 6H), 3.63 (s, 4H), 7.19–7.31 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 37.1, 58.6, 127.0, 128.3, 129.0, 137.9, 144.1. MS (EI) *m/z*: 332 (M^+, 6), 241 ($M^+ - CH_2Ph$, 68), 91 ($PhCH_2^+$, 100). MS (CI, NH_3) *m/z*: 333 ($M^+ + H$, 100).

Thermolysis of 5*b* in presence of dichloromaleic anhydride

A solution of **5***b* (0.2046 g, 0.8106 mmol) and dichloromaleic anhydride (0.150 g, 0.898 mmol) in benzene (10 mL) was heated overnight at 80°C in a sealed tube. Removal of the solvent and Kugelrohr distillation of the residue gave a yellow crystalline product, 3,4-dichloro-6-benzylthio-6-methoxy-2*H*-pyran-2,5-(6*H*)-dione (**17***b*), mp 69–70°C, 75%. The product did not survive an attempt at chromatography on silica gel. IR (CCl_4) cm^{-1}: 3087, 3032, 2949, 2894, 2840, 1762s, 1721s, 1583s, 1497, 1457, 1414, 1273m, 1234m, 1196m, 1163s,

1040, 982m, 908, 885, 701s, 666m. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.54 (s, 3H), 3.75 (s, 2H), 7.29 (s, br, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 35.0, 52.5, 108.9, 127.7, 128.7, 129.1, 135.0, 136.8, 141.3, 152.6, 173.5. MS (EI) *m/z*: 337 (3), 335 (7), 333 (10) (M^+ + H), 259 (18), 214 (11), 212 (65), 210 (94), 185 (13), 183 (70), 181 (100), 123 (23), 91 (20). MS (CI, NH_3) *m/z*: 354 (16), 352 (65), 350 (100) ($M^+ + NH_4$), 337 (8), 335 (25), 333 (35), (M^+ + H).

Thermolysis of 5*c* in benzene

A solution of **5***c* (0.1629 g, 0.856 mmol) in benzene (ca. 1 mL) was sealed into an NMR tube. Thermolysis at 60°C, followed by ^{1}H NMR spectroscopy, gave $k(60°C) = 2.1 \times 10^{-5}$ s^{-1}. Acetone and the diastereomeric 1,2-bis(ethylthio)-1,2-dimethoxyethenes were predominant products. Separation of the latter (Chromatotron, hexane) gave *E*-1,2-bis(ethylthio)-1,2-dimethoxyethene (**7***c*, 0.0304 g, 38%) and the *Z* isomer (**8***c*, 0.0250 g, 27%) as clear liquids.

E-*1,2-Bis(ethylthio)-1,2-dimethoxyethene* (**7**c): IR (GC/FTIR) cm^{-1}: 2976m, 2940s, 2887, 2832, 1457 br, 1383, 1310, 1267, 1188, 1079 br, 975, 937, 904, 825, 762, 712. Raman (neat) cm^{-1}: 1581.4, 653.4. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.25 (t, *J* = 7.3 Hz, 6H), 2.66 (q, *J* = 7.3 Hz, 4H), 3.61 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 15.1, 25.4, 58.0, 143.1. MS (EI) *m/z*: 208 (M^+, 15), 193 ($M^+ - CH_3$, 4), 179 ($M^+ - CH_2CH_3$, 29), 165 (13), 135 (3), 49 (100). MS (CI, NH_3) *m/z*: 209 (M^+ + H).

Z-1,2-Bis(ethylthio)-1,2-dimethoxyethene (**8**c): IR (GC/FTIR) cm^{-1}: 2972, 2939m, 2887, 2836, 1579, 1457, 1381, 1265, 1194s, 1114 br, 1026, 967, 863, 764. Raman (neat) cm^{-1}: 1596, 655.7. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.27 (t, *J* = 7.3 Hz, 6H), 2.65 (q, *J* = 7.3 Hz, 4H), 3.68 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 14.7, 26.4, 58.8, 143.4. MS (EI) *m/z*: 208 (M^+, 83), 193 ($M^+ - CH_3$, 15), 179 ($M^+ - CH_2CH_3$, 100), 165 (44), 135 (2). MS (CI, NH_3) *m/z*: 209 (M^+ + H).

Thermolysis of 5*c* in the presence of dichloromaleic anhydride

A solution of **5***c* (0.197 g, 1.03 mmol) in benzene (10 mL) containing dichloromaleic anhydride (0.190 g, 1.14 mmol) was heated at 70°C overnight. Kugelrohr distillation of the residue left after removal of the solvent afforded **17***c*, mp 71–74°C. IR (CCl_4) cm^{-1}: 2950, 2881, 1807, 1761s, 1722m, 1583, 1458, 1266, 1236, 1196, 1160m, 1102, 1040s, 982, 909, 886, 827, 667, 527, 478. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.24 (t, *J* = 7.5 Hz, 3H), 2.52 (dq, *J* = −12.8 Hz, 7.5 Hz, 1H), 2.60 (dq, *J* = −12.8, 7.5 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 13.6, 24.7, 52.5, 109.0, 136.6, 141.2, 152.7, 173.6. MS (EI) *m/z*: 275 (M^+ + H, 2), 273 (M^+ + H, 4), 271 (M^+ + H, 6), 235 ($M^+ - {}^{35}Cl$, 6), 213 (13), 211 (28), 209 (19), 185 (20), 183 (73), 181 (100). MS (CI, NH_3) *m/z*: 292 (4), 290 (13), 288 (20), ($M^+ + NH_4$), 275 (20), 273 (95), 271 (100), (M^+ + H).

Thermolysis of 5*d* in benzene

A solution of **5***d* (0.37 g, 2.1 mmol) in benzene (15 mL) was refluxed overnight. Chromographic separation of the products (Chromatotron, 2 mm plate, hexane) gave the *E* and *Z* dimers of (methoxy)methylthiocarbene, 0.1225 g (32%) and 0.1005 g (27%), respectively, both oils.

E-*1,2-Bis(methylthio)-1,2-dimethoxyethene* (**7**d): IR (GC/FTIR) cm^{-1}: 3005, 2963, 2938m, 2909, 2839, 1445, 1319, 1203s, 1143s, 1023s, 960, 807. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.20 (s, 6H), 3.63 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 14.5, 58.2, 142.8. MS (EI, GC/MS) *m/z*: 180 (M^+, 10), 165 ($M^+ - CH_3$, 22), 137 ($M^+ - CH_3CO$, 74), 75 (100). MS (CI, NH_3) *m/z*: 181 (M^+ + H).

Z-1,2-Bis(methylthio)-1,2-dimethoxyethene (**8**d): IR (GC/FTIR) cm^{-1}: 3002, 2938m, 2838, 1584, 1445, 1315, 1194s, 1115 br, 1030, 964, 866. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.21 (s, 6H), 3.68 (s, 6H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 15.3, 58.8, 143.0. MS (EI, GC/MS) *m/z*: 180 (M^+, 10), 165 ($M^+ - CH_3$, 23), 137 ($M^+ - CH_3CO$, 79), 75 (100). MS (CI, NH_3) *m/z*: 181 (M^+ + H).

Thermolysis of 5*d* in the presence of dichloromaleic anhydride

A solution of **5***d* (0.2077 g, 1.18 mmol) and dichloromaleic anhydride (0.22 g, 1.3 mmol) in benzene (10 mL) was kept at 80°C, overnight, in a sealed tube. Evaporation of the solvent and Kugelrohr distillation of the residue gave 0.2575 g of **17***d* (85%) as a yellow solid, mp 89–91°C. IR (CCl_4) cm^{-1}: 3502, 2995, 2948, 2839, 1805m, 1762s, 1721s, 1631, 1584s, 1460, 1436, 1271s, 1236s, 1196s, 1162 br, 1042 br, 962, 909, 887, 826, 670m, 596, 526. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.06 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 12.9, 52.2, 108.6, 136.5, 141.2, 152.6, 172.7. MS (EI) *m/z*: 256 (M^+, 2), 225 ($M^+ - OCH_3$, 2), 223 (5), 221 ($M^+ - {}^{35}Cl$, 15), 213 (3), 211 (13), 209 ($M^+ - SCH_3$, 18), 199 (13), 197 (18), 185 (9), 183 (45), 181 (71). MS (CI, NH_3) *m/z*: 278 (6), 276 (20), 274 (28), 261 (15), 259 (56), 257 (100). Structure **17***d* was confirmed by single crystal X-ray diffraction.

Thermolysis of 2,2-dimethoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline in the presence of phenyl isocyanate

A solution of the oxadiazoline (4) (0.010 g, 0.063 mmol) and phenyl isocyanate (0.051 g, 0.43 mmol) in benzene (0.5 mL) was degassed by means of freeze–pump–thaw cycles and sealed under vacuum into a glass tube. The tube was immersed in an oil bath, kept at 100°C, for 4 days. It was then opened, and the volatiles were distilled off under vacuum, with the maximum pot temperature limited to 100°C. The residue was chromatographed (Chromatotron, silica, hexanes) on a plate that had been pretreated with triethylamine in hexanes (1:20). The yield of the Hoffmann hydantoin (2) was 65% (by ^{1}H NMR), mp 131–132°C (lit. (2) mp 129–130°C).

5,5-Dimethoxy-1,3-diphenyl-2,4-imidazolidinedione (hydantoin): ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.56 (s, 6H), 7.24–7.57 (m, 8H), 7.61 (d, *J* = 1.5 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 52.5, 103.9, 125.3, 126.1, 127.2, 128.6, 129.0, 129.1, 130.5, 133.2, 152.3, 165.3. MS (EI) *m/z*: 281 (M^+ − OMe), 193, 165, 116. The ^{13}C NMR spectrum is in excellent agreement with that reported by Hoffmann et al. (*2b*) for the analogue from *p*-tolyl isocyanate.

Thermolysis of 5*d* in the presence of phenyl isocyanate

A solution of **5***d* (0.50 g, 2.4 mmol) and phenyl isocyanate (0.63 mL, 5.8 mmol) in benzene (25 mL) was refluxed under N_2 for 16 h. The benzene was evaporated and methanol was

added (stirring for 1 h) to destroy excess isocyanate. Excess methanol was evaporated and the residue was chromatographed. Three products, a 2:1 adduct (**18***d*, 8%) and diastereomeric 2:2 adducts (**19***d*, 34%, mp 181–182°C (MeOH), diastereomer ratio 2:1) were found.

*3-Methoxy-3-methylthio-1-phenylcarbamoyloxindole (**18**d)*: Melting point 106–108°C. IR (CCl_4) cm^{-1}: 3298 br, 3259 br, 3145, 3082, 2959, 2931, 1748s, 1601s, 1553s, 1501, 1466m, 1448m, 1339m, 1311, 1277m, 1242m, 1209, 1166m, 1154, 1108m, 1087, 1024, 691, 677, 575, 506. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.38 (s, 3H), 3.43 (s, 3H), 7.14–7.61 (m, 9H), 8.37 (d, J = 8.0 Hz, 1H), 10.48 (br, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 10.9, 53.1, 117.0, 120.6, 124.4, 124.7, 125.1, 129.1, 131.2, 136.9, 138.8, 149.1, 174.1. MS (EI) *m/z*: 328 (M^+, 6), 281 ($M^+ - SCH_3$, 48), 207 (4), 162 (100), 146 (6), 119 (24). MS (CI, NH_3): 346 ($M^+ + NH_4$, 14), 329 ($M^+ + H$, 17).

Major diastereomer of oxindole **19**d: IR (CCl_4, υ_{max}) cm^{-1}: 3414 br, 3061, 2931, 2832, 1746s, 1604m, 1525s, 1465, 1442m, 1338, 1309, 1279, 1243, 1196, 1180, 1117, 1095 br, 1073, 690. ^1H NMR (200 MHz, $CDCl_3$) δ: 2.12 (s, 3H), 2.39 (s, 3H), 3.33 (s, 3H) 3.54 (s, 3H). Minor diastereomer: 2.13 (s, 3H), 2.36 (s, 3H), 3.40 (s, 3H), 3.53 (s, 3H); composite signals: 7.08–7.61 (m), 8.23 (s, br), 8.41 (s, br). ^{13}C NMR of 2:1 mixture (50 MHz, $CDCl_3$) δ: 10.8, 12.5, 51.2, 51.3, 53.4, 53.9, 82.6, 83.1, 96.6, 96.7, 109.0, 110.0, 111.0, 112.4, 112.8, 119.8, 119.9, 123.9, 124.6, 124.7, 124.9, 125.1, 129.1, 129.2, 130.8, 136.4, 136.6, 140.1, 162.9, 163.1, 172.9. MS (EI) *m/z*: 387 (M^+ − OMe, 4), 371 (M^+ − SMe, 85), 343 (100), 298 (10), 270 (40), 210 (45), 208 (99), 162 (94), 119 (19), 77 (20). MS (CI, NH_3) *m/z*: 436 ($M^+ + NH_4$).

Thermolysis of 5*d* in the presence of dimethyl acetylenedicarboxylate

A solution of **5***d* (0.329 g, 1.87 mmol) and DMAD (0.46 mL, 3.7 mmol) in benzene (20 mL) was heated at 70°C for 16 h in a sealed tube. Thin-layer chromatography of the residue left after removal of the benzene showed five compounds. Only three of them were characterized, a minor compound that had the NMR properties expected for dihydrofuran **11**, and an inseparable mixture of diastereomers **14**.

*2-Methoxy-5,5-dimethyl-2-methylthio-3,4-bis(methoxycarbonyl)-2,5-dihydrofuran (**23**)*: Clear liquid, 6% yield. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.54 (s, 3H), 1.57 (s, 3H), 2.11 (s, 3H), 3.48 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 13.1, 26.0, 27.3, 51.3, 52.5, 52.7, 88.5, 116.7, 137.7, 141.8, 162.2, 163.0.

cis- *and* trans-*2,5-Dimethoxy-3,4-bis(methoxycarbonyl)-5-[methyl(3-propiolato)]-2-methylthio-2,5-dihydrofuran (**14**, 10%)*: Isomer ratio 1.7:1.0; spectroscopic properties those of the mixture. IR (CCl_4) cm^{-1}: 3008, 2952, 2894, 2839, 1730 br, 1681, 1458, 1436, 1328, 1266 s, 1235 m, 1183, 1116, 1098, 1077, 1038, 1020, 988, 956, 918, 873, 692, 578. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.12 (s), 2.13 (s), 3.49 (s), 3.62 (s), 3.63 (s), 3.81 (s), 3.85 (s), 3.91 (s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 12.4, 12.6, 52.8, 52.9, 53.0, 53.1, 77.9, 78.1, 78.3, 78.6, 102.1, 118.8, 132.9, 133.0, 143.1, 143.3, 152.8, 159.5, 159.6, 161.7. MS (EI) *m/z*: 374 (M^+, 2), 343 (9), 327 (100), 315 (7), 157 (61), 59 (22). MS (CI, NH_3): 392 ($M^+ + NH_4$, 7), 375 ($M^+ + H$, 8).

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