Synthesis and spectra of aldehyde- and ketone-*O*-(2,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oximes — Thermal sources of some methoxy(oximino)carbenes

Arkadiusz Klys, Malgorzata Dawid, and John Warkentin

Abstract: Ten new oxadiazoline sources of methoxy(oximino)carbenes were synthesized by exchanging the acetoxy group of 2-acetoxy-2-methoxy-Δ^3-1,3,4-oxadiazoline with an oximino group. The new compounds were characterized by means of spectroscopy and the formation of carbenes upon thermolysis of a few was demonstrated by means of interception with *tert*-butyl alcohol. The carbenes fragmented to form methoxycarbonyl and iminyl radicals.

Key words: 2,2-dioxyoxadiazoline, methoxy(oximino)carbene, oxadiazole, radical pair, rearrangement.

Résumé : On a effectué la synthèse de 10 nouvelles oxadiazolines sources de méthoxy(oximino)carbènes en procédant à l'échange du groupe acétoxy de la 2-acétoxy-2-méthoxy-Δ^3-1,3,4-oxadiazoline avec un groupe oximino. On a caractérisé les nouveaux composés par spectroscopie et la formation de carbènes par thermolyse de quelques-unes de ces sources a été mise en évidence par leur interception par l'alcool *tert*-butylique. Les carbènes se fragmentent avec formation des radicaux méthoxycarbonyle et iminyle.

Mots clés : 2,2-dioxyoxadiazoline, méthoxy(oximino)carbène, oxadiazole, paire de radicaux, réarrangement.

[Traduit par la Rédaction]

Introduction

Some 2,5-dihydro-5,5-dimethyl-2,2-dioxy-1,3,4-oxadiazoles (**1a**–**1d**) (also known as 5,5-dimethyl-2,2-dioxy-Δ^3-1,3,4-oxadiazolines) have been shown to be versatile reagents for the generation of carbenes including alkoxymethoxy-, acetoxymethoxy-, alkoxyaryloxy-, and diaryloxycarbenes. (1) Having shown that an alkyne functional group in the carbene from **1e** (2) and a carbonyl group in the carbene from **1f** (3) can intercept a dialkoxycarbene in an intramolecular reaction, leading to interesting products, and that thiocarbonyl groups are effective interceptors in intermolecular reactions (4), we decided to try the oxadiazoline approach to generate carbenes containing other functional groups (Scheme 1).

We now report the preparation of some aldehyde and ketone-*O*-(2,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oximes (**2**) (also known as corresponding oxadiazolinyl oximes) that are precursors of carbenes of type **3** (Scheme 2), and show that carbenes **3d** and **3e** are indeed generated by thermolysis of **2d** and **2e**. Some potential intramolecular reactions of a generalized carbene **3** are shown in Scheme 3.

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Methods, results, and discussion

Compounds **2** were prepared by the exchange method (5), from 2-acetoxy-2-methoxy-2,5-dihydro-5,5-dimethyl-1,3,4-oxadiazole (also known as 2-acetoxy-2-methoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline) (**4**) and the appropriate oxime (**5**) in the presence of catalytic *p*-toluenesulfonic or trifluoroacetic acid (Scheme 4). All of the oximes used in this work are known compounds and compounds **2**, with the exception of **2b**, were the (*E*)-isomers. In the case of **2b**, a mixture of (*E*)- and (*Z*)-isomers was obtained. They were not separated and the ^{13}C NMR spectrum of the major isomer was assigned on the basis of signal intensities.

The oximes **5** were prepared by standard methods, including the (*Z*)-oxime of benzaldehyde (6). Exchange with the latter gave the same product (**2c**) as that obtained with the (*E*)-oxime of benzaldehyde, indicating that the oxime isomerizes under the acidic exchange conditions or that the product isomerizes after exchange has occurred (or both). To date we have been unable to prepare analogues of **2** with a (*Z*)-aldoxime unit.

Structural assignments are based on ^{1}H and ^{13}C NMR spectra, as well as high-resolution mass spectra of more complex samples. In some cases, the connectivity was supported with gradient HSQC spectra, to correlate ^{1}H and ^{13}C NMR chemical shifts. The ^{13}C NMR spectra of 2,2-

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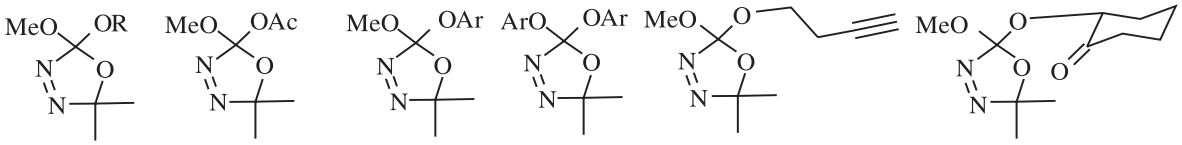
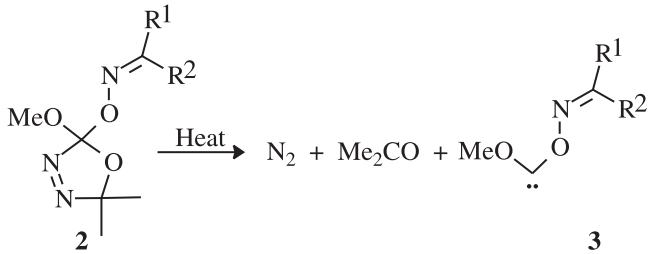
Scheme 1.



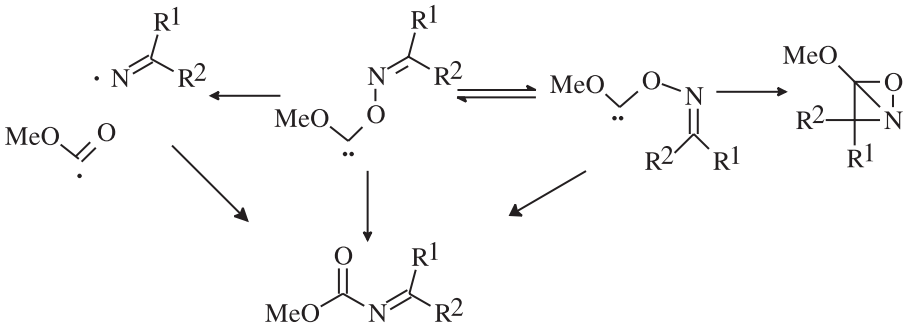
1a **1b** **1c** **1d** **1e** **1f**

Scheme 2. For **2a** and **3a**: $R^1 = R^2 = Me$; **2b** and **3b**: $R^1 = Et$, $R^2 = Me$ (major), $R^1 = Me$, $R^2 = Et$ (minor); **2c** and **3c**: $R^1 = Ph$, $R^2 = H$; **2d** and **3d**: $R^1 = Ph$, $R^2 = Me$; **2e** and **3e**: $R^1 = R^2 = Ph$; **2f** and **3f**: CR_1R_2 = 9-fluorenylidene; **2g** and **3g**: $R_1R_2 = (PhCH)_4$; **2h** and **3h**: $R^1R^2 = (CH_2)_4$; **2i** and **3i**: $R_1R_2 = (CH_2)_5$; **2j** and **3j**: $R^1 = MeCO$, $R^2 = Me$.

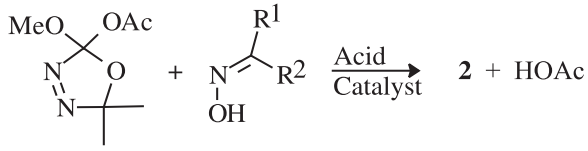


2 **3**

Scheme 3.



Scheme 4.



4 **5**

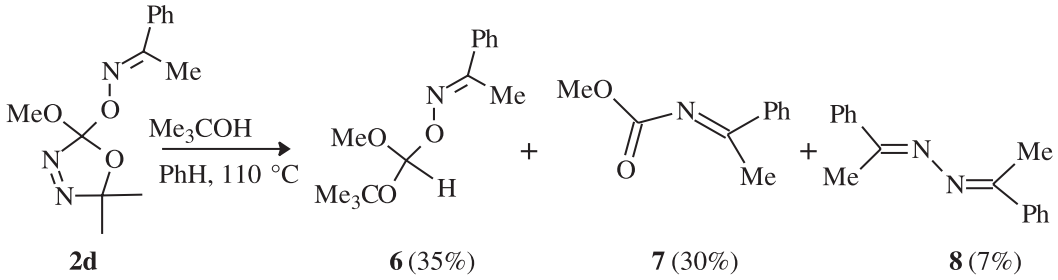
dialkoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazolines have the C-2 and C-5 signals near 137 and 119 δ, respectively (7). Values of the ^{13}C NMR chemical shift of iminyl carbons in 25 ketoximes fall between δ = 157.7 and 170.1 (8).

IR spectra were generally not informative enough to provide strong evidence of structure, with a weak band attributed to C=N stretching (9) near 1650 cm^{-1}. The carbonyl frequency of **2j**, as well as strong fingerprint bands for a few of the compounds **2** are included.

To test for the intermediacy of a carbene **3**, the potential precursor **2** was thermolysed in dry benzene, and in benzene containing *tert*-butyl alcohol (1.05 mol/L). Compounds chosen for initial study, namely **2d** and **2e**, are members of the family **2** with unsaturation in the group(s) attached to the iminyl carbon.

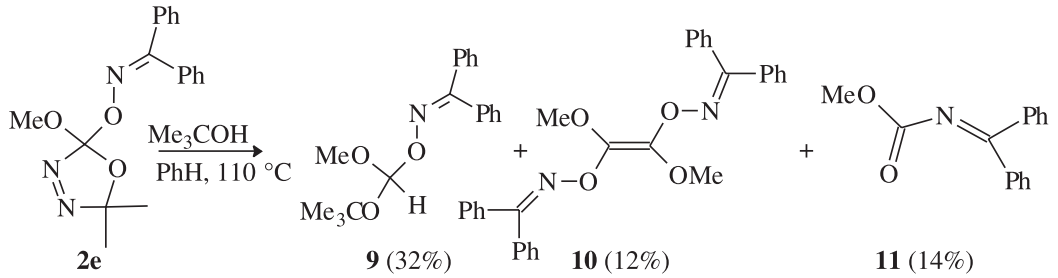
Thermolysis of **2d** in benzene containing *tert*-butyl alcohol (1.05 mol/L) gave **6** (35%) and **7** (30%) as major products. Acetophenone azine was also isolated. Capture of a carbene intermediate by the alcohol would afford **6**, while intramolecular rearrangment, by 1,2-migration of the iminyl function, or fragmentation to radicals and radical pair coupling, would lead to **7** (Scheme 5). There is precedent for the capture of carbenes by alcohols (10), and for rearrangement of acyloxycarbenes (1*f*, 11), which are models for **3**. Concerted rearrangement of carbene **3d** to **7** need not necessarily involve a large rate constant, even though rearrangement competed with bimolecular capture by *tert*-butyl alcohol. Capture of dimethoxycarbene by alcohols, in acetonitrile at room temperature, occurs with pseudo-first-order rate constants lying between about 10^4 s^{-1} (ethanol) and 10^5 s^{-1} (methanol) (10*a*). Capture occurs by protonation to form an ion pair, and would be slowed in benzene, accelerated by the higher temperature used in this work, and probably slowed for *tert*-butyl alcohol, given that ethanol reacts more slowly than methanol.

Scheme 5.

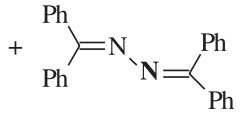


2d **6** (35%) **7** (30%) **8** (7%)

Scheme 6.



2e **9** (32%) **10** (12%) **11** (14%)



12 (5%)

Alternatively, **7** could arise by coupling of the methoxycarbonyl- and methylphenyliminyl radical pair. Some dialkoxycarbenes have been shown to fragment to radical pairs at 110 °C (10*d*, 12). The fact that acetophenone azine was isolated means that the radical-pair mechanism plays some role because the azine is almost certainly derived from coupling of the appropriate iminyl radicals. The fraction of **7** that arises by that route, as opposed to intramolecular rearrangement of **3d**, is not known at this time.

Compound **2e** afforded four products (**9**–**12**) when thermolysed in benzene containing *tert*-butyl alcohol (1.05 mol/L). Orthoformate **9** (32%) is the product of capture of carbene **3e** with *tert*-butyl alcohol while compound **10** (12%) is the carbene dimer and **11** (14%) appears to be the product of a 1,2-migration of the diphenyliminyl group to the carbene site of **3e**, either in a concerted intramolecular rearrangement or by means of coupling of methoxycarbonyl radicals and diphenyliminyl radicals (Scheme 6).

Analogous rearrangements, which are known for some acyloxycarbenes (1*f*, 11), appear to be concerted, in general. In the present case, the formation of diphenyliminyl radicals is strongly implied by the finding of compound **12**, which is most likely the product of coupling of the latter radicals. This conclusion was reinforced when thermolysis of **2e** in the presence of dimethyl acetylenedicarboxylate (DMAD) gave a mixture of products from which **13** was isolated. Presumably, **13** arose from intramolecular, radical aromatic substitution following addition of the diphenyliminyl radical to DMAD. Thus, the rearrangement of **3e** occurred, at least in part, by the carbene homolysis – radical combination mechanism.

There isn't any evidence for or against intramolecular addition of carbenes **3** to the iminyl functional group to generate the bicyclic intermediate of Scheme 3. Survival of such materials at 110 °C is unlikely, and alternative methods for generating carbenes **3** at lower temperatures will need to be investigated.

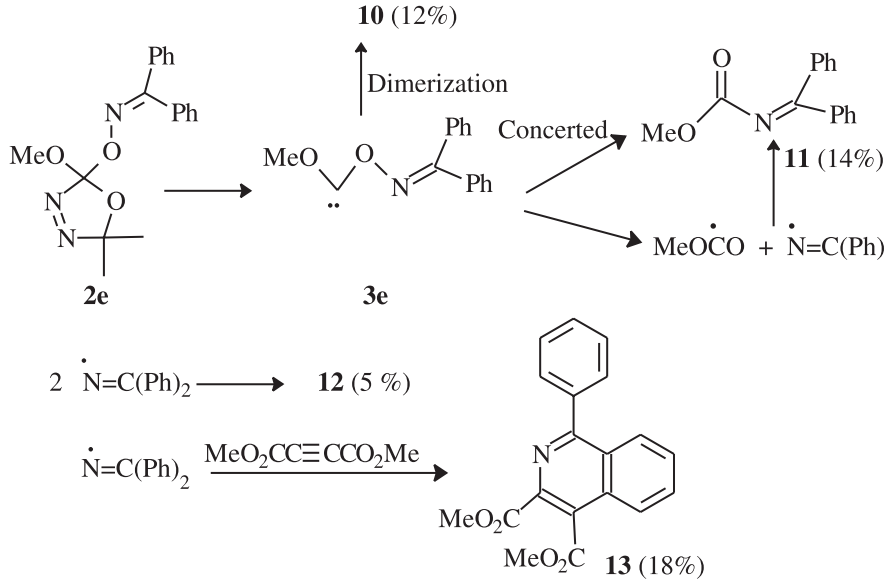
Summary

Ten new oxadiazolines, with a methoxy and an oximino substituent at C-2, were prepared and characterized. All of them can be expected to afford methoxy(oximino)carbenes upon thermolysis in benzene, as demonstrated for two of them by means of trapping with *tert*-butyl alcohol. In the absence of the alcohol a carbene dimer, as well as products from carbene fragmentation to a radical pair, were isolated (Scheme 7).

Experimental

IR spectra were taken with a Bruker Tensor 27 FT-IR instrument equipped with a Harrick ATR accessory and a ZnSe crystal. Neat samples in the solid or liquid state were used. NMR spectra were obtained with Bruker AV 200 or AV 600 instruments and, in one case, with a Varian Geminii 200BB machine. ^{1}H NMR chemical shifts in $CDCl_3$ and in C_6D_6 were referenced to the signal from $CHCl_3$ at δ =

Scheme 7.



7.26 ppm and the C_6HD_5 signal at 7.16 ppm, respectively. ^{13}C NMR shifts for solutions in $CDCl_3$ were referenced to the center line of the $CDCl_3$ triplet at δ = 77.16 ppm. Mass spectra were taken with a Micromass (Waters) GCT, TOF mass spectrometer, with ammonia for CI spectra. Most of the oxadiazolines gave $(M + H)^+$ masses, as well as the base peak corresponding to the 2-methoxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazolinyl species ($C_5H_9N_2O_2$). A few did not afford $(M + H)^+$ masses, but gave the base peak instead. The mass corresponding to loss of N_2 was not generally observed.

Synthesis

The standard procedure involved 20 mmol of the acetoxymethoxyoxadiazoline (**4**) in methylene chloride containing a catalytic amount of toluenesulfonic acid and 20 mmol of the relevant oxime, except in the case of the preparation of **2g**, where the oxime was used in fourfold excess. The solution was kept at room temperature for 2 days before aq. KOH (5 mL H_2O plus ca. 0.4 g of KOH) was added and the resulting two-phase mixture was left for 1 day, except in the case of **2d**, which is rapidly destroyed by strong base. In that case, the catalytic acid and acetic acid were removed by means of a quick extraction with aq. $NaHCO_3$. After separation of the phases, washing with water, and drying with Na_2SO_4, the solvent was evaporated and the residue was column chromatographed on SiO_2 with 10% EtOAc in hexane for elution. The first fraction to be eluted was always the oxadiazoline. Yields (unoptimized) were about 40% in all cases except for **2g**, which was obtained in 15%–25% yield.

Acetone-O-(2,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oxime (2a)

Colourless oil. ^1H NMR (200.1 MHz, $CDCl_3$) δ: 1.56 (s, 3H), 1.61 (s, 3H), 1.87 (s, 3H), 1.95 (s, 3H), 3.60 (s, 3H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 15.58, 21.40, 22.55, 24.13, 52.26, 119.91, 137.69, 158.65. MS (CI, NH_3) *m/z*: calcd. for $C_8H_{16}N_3O_3$ $(M + H)^+$: 202.23; found: 202.2.

2-Butanone-O-(1,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oximes (2b) (E/Z mixture, not separated except for ^{13}C NMR of the major isomer)

Colourless oil. IR (most intense peaks, cm^{-1}): 1165, 1112, 898. ^1H NMR (600 MHz, $CDCl_3$) (major : minor isomer ratio ca. 2.5:1, integrations separate for each isomer) δ: (major isomer) 1.028 (t, *J* = 7.6 Hz, 3H), 1.556 (s, 3H), 1.625 (s, 3H), 1.933 (s, 3H), 2.191 (q, *J* = 7.6 Hz, 2H), 3.629 (s, 3H); (minor isomer) 1.087 (t, 3H), 1.558 (s, 3H), 1.611 (s, 3H), 1.845 (s, 3H), 2.418 (m, 2H), 3.608 (s, 3H). ^{13}C NMR (200 MHz, $CDCl_3$) (major isomer) δ: 10.62, 14.67, 19.52, 23.21, 24.22, 29.46, 52.95, 120.50, 163.10. HR-MS (CI, NH_3) *m/z*: calcd. for $C_9H_{18}N_3O_3$ $(M + H)^+$: 216.1348; found: 216.1345.

Benzaldehyde-O-(1,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)(E)-oxime (2c)

White solid, mp 65 °C. ^1H NMR (200.1 MHz, $CDCl_3$) δ: 1.60 (s, 3H), 1.69 (s, 3H), 3.69 (s, 3H), 7.33-7.55 (m, 5H), 8.23 (s, 1H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 23.22, 24.87, 53.12, 121.22, 127.71, 128.88, 130.89, 131.09, 138.31, 152.51. HR-MS (CI, NH_3) *m/z* calcd. for $C_{12}H_{16}N_3O_3$ $(M + H)^+$: 250.1192; found: 250.1171.

Acetophenone-O-(1,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oxime (2d)

Colourless oil. IR (most-intense peaks, cm^{-1}): 1166.0, 1109.3, 904.8, 762.3, 693.5. ^1H NMR (200.1 MHz, $CDCl_3$) δ: 1.59 (s, 3H), 1.65 (s, 3H), 2.36 (s, 3H), 3.71 (s, 3H), 7.33–7.36 (m, 3H), 7.53–7.58 (m, 2H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 13.53, 23.12, 24.89, 53.13, 120.97, 126.52, 128.50, 129.90, 135.62, 138.51, 158.68. In the *E*-oxime itself, the chemical shift of the iminyl carbon ($CDCl_3$) is 155.9 δ (8). HR-MS (CI, NH_3) *m/z* calcd. for $C_{13}H_{18}N_3O_3$ $(M + H)^+$: 264.1348; found: 264.1361.

Benzophenone-O-(1,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oxime (2e)

Colourless solid, mp 63 to 64 °C. IR (strongest sig-

nals, cm^{-1}: 1028.26, 923.09, 700.03. ^1H NMR (200.1 MHz, $CDCl_3$) δ: 1.58 (s, 3H), 1.68 (s, 3H), 3.54 (s, 3H), 7.29–7.44 (m, 10H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 23.21, 24.96, 53.16, 121.02, 128.17, 128.34, 128.47, 129.26, 130.16, 132.60, 135.59, 160.73. HR-MS (CI, NH_3) *m/z* calcd. for $C_{18}H_{21}N_3O_3$ $(M + H)^+$: 326.1505; found: 326.1482.

Fluorenone*-O-*(1,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oxime (2f)

Pale yellow solid, mp 105 to 106 °C. IR (most intense peaks, cm^{-1}): 1166.18, 1098.28, 899.09. ^1H NMR (600 MHz, $CDCl_3$) δ: 1.65 (s, 3H), 1.78 (s, 3H), 3.81 (s, 3H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.36, 7.33 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 8.33 (d, *J* = 7.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 23.27, 24.94, 53.47, 120.13, 120.17, 121.80, 122.41, 128.17, 128.59, 129.99, 130.35, 130.91, 132.01, 135.00, 138.80, 140.88, 142.13, 155.33. HR-MS (CI, NH_3) *m/z* calcd. for $C_{18}H_{18}N_3O_3$ $(M + H)^+$: 324.1348; found: 324.1331.

2,3,4,5-Tetraphenylcyclopentadienone*-O-*(1,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oxime (2g)

Reddish foam. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.05 (s, 3H), 1.38 (s, 3H), 3.03 (s, 3H), 6.73–6.85 (m, 4H), 6.99–7.27 (m, 16H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 21.99, 25.10, 53.30, 121.60, 124.69, 126.75, 126.98, 127.21, 127.47, 127.61, 127.76, 130.01, 130.08, 130.66, 131.32, 132.66, 132.51, 132.66, 133.60, 134.05, 136.30, 138.16, 145.61, 151.57, 160.88. HR-MS (CI, NH_3) *m/z* calcd. for $C_{34}H_{29}N_3O_3$: 527.2209; found: 527.2213.

Cyclopentanone*-O-*(1,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oxime (2h)

Colourless oil. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.57 and 1.62 (2s, superimposed on m, total 10H), 2.18 (m, 2H), 2.53 (m, 2H), 3.60 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 23.19, 24.77, 25.48, 25.70, 25.99, 26.82, 32.18, 52.86, 120.34, 138.46, 164.34. MS (CI, NH_3) *m/z* calcd. for $C_5H_9N_2O_2$ $(M - C_5H_8NO)^+$: 129.14; found: 129.1 (100%).

Cyclohexanone*-O-*(1,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)oxime (2i)

Colourless oil. IR (C=N and four most intense peaks, cm^{-1}): 1763.2, 1164.3, 1101.8, 897.8, 862.3. ^1H NMR (600 MHz, $CDCl_3$) δ: 1.57 (s, 3H), 1.61 (s, 3H), 1.70–1.80 (m, 6H), 2.36 (distorted t, 2H), 2.52 (distorted t, 2H), 3.59 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 23.33, 24.70, 25.23, 28.43, 31.31, 52.87, 120.49, 125.67, 138.29, 171.14. MS (CI, NH_3) *m/z* calcd. for $C_5H_9N_2O_2$ $(M - C_6H_{10}NO)^+$: 129.14; found: 129.1 (100%).

Biacetyl*-O-*(1,5-dihydro-2-methoxy-5,5-dimethyl-1,3,4-oxadiazol-2-yl)]monoxime (2j)

Colourless oil. IR (neat, cm^{-1}): 1702.4 (C=O), 913.3 (most intense fingerprint peak). ^1H NMR (200.2 MHz, $CDCl_3$) δ: 1.59 (s, 3H), 1.67 (s, 3H), 2.05 (s, 3H), 2.28 (s, 3H), 3.70 (s, 3H). ^1H NMR (200.2 MHz, C_6D_6) δ: 1.27 (s, 3H), 1.40 (s, 3H), 1.76 (s, 3H), 1.90 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 9.54, 23.30, 24.81, 25.59, 53.35, 99.78, 147.40, 188.23, 220.02. MS (CI, NH_3) *m/z* calcd. for $C_9H_{16}N_3O_4$ $(M + H)^+$: 230.24; found: 230.1.

Thermolysis procedure

The oxadiazoline (1.5 mmol) in 5 mL of benzene, added to 5.25 mmol of *tert*-butyl alcohol, was heated in a sealed vessel at 110 °C for 24 h. The tube was then opened, and the solvent and volatile products were evaporated with a rotary evaporator. The residue was column chromatographed on silica gel with petroleum ether – ethyl acetate as the eluent. Some fractions had to be rechromatographed on a 2 mm silica plate in a Chromatotron apparatus, with the same solvents for elution. Thermolysis of **2d** afforded products **6**–**8**. The carbene dimer was not found.

Acetophenone*-O-(tert-*butoxy)(methoxymethylene)oxime (6)

Colourless oil, yield 35%. ^1H NMR (600 MHz, $CDCl_3$) δ: 1.35 (s, 9H), 2.29 (s, 3H), 3.42 (s, 3H), 6.00 (s, 1H), 7.35–7.36 (m, 3H), 7.65–7.67 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.48, 14.27, 28.97, 31.74, 51.31, 113.90, 126.42, 128.51, 129.43, 156.07.

Methyl (phenylethylidene)carbamate (7)

Colourless oil, in 30% yield. ^1H NMR (600 MHz, $CDCl_3$) δ: 2.39 (s, 3H), 3.92 (s, 3H), 7.39–7.45 (m, 3H), 7.72–7.73 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 13.88, 54.81, 126.53, 128.12, 130.15, 134.09, 153.99 (C=N), 162.22 (C=O).

Acetophenone azine (8) (13)

Yield: 7%. ^1H NMR (200.2 MHz, $CDCl_3$) δ: 2.33 (s, 6H), 7.42–7.45 (m, 6H), 7.91–7.93 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 15.25, 126.82, 128.51, 129.83, 138.51, 158.15. HR-MS (CI, NH_3) *m/z* calcd. for $C_{16}H_{16}N_2$: 236.1313; found: 236.1313 and 237.1387 $(M + H)^+$.

Thermolysis of **2e** afforded benzophenone-*O*-(*tert*-butoxy)(methoxymethylene)oxime (**9**), the carbene dimer (**10**), methyl (diphenylmethylene)carbamate ($MeOCON{=}CPh_2$, **11**) (14), and benzophenone azine (**12**, 5%) (15).

Benzophenone*-O-(tert-*butoxy)(methoxymethylene)oxime (9)

Compound **9** was very susceptible to hydrolysis and was not obtained in a pure state. Yield: ca. 32%. ^1H NMR (200.2 MHz, $CDCl_3$) δ: 1.29 (s, 9H), 3.40 (s, 3H), 5.99 (s, 1H), 7.31–7.52 (m, 10H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 28.92, 51.38, 114.01, 128.02–129.58 (eight signals visible in this range, but not resolved). A meaningful mass spectrum could not be obtained.

1,2-Dimethoxy-1,2-(diphenyliminoxy)ethene (10)

Colourless oil, yield 12%. ^1H NMR (200.2 MHz, $CDCl_3$) δ: 3.66 (s, 6H), 7.33–7.27 (m, 10H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 55.40, 128.45, 128.55, 129.03, 129.17, 129.94, 131.08, 132.20, 134.70, 154.67, 164.63. A correlation between the ^1H and ^{13}C NMR signals was established by means of gradient HSQC spectra. The trans isomer was assumed.

Methyl (diphenylmethylene)carbamate (11) (14)

Pale yellow oil, yield 14%. ^{1}H NMR (200.2 MHz, $CDCl_3$) δ: 3.86 (s, 3H), 7.33–7.59 (m, 10H). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ: 53.26, 128.46, 129.10, 131.30, 136.48, 163.31 (C=O), 171.55 (C=N). The signals at 128.46 and 129.10 are much more intense than the other ArH signals, and probably correspond to several coincident chemical shifts.

Dimethyl 1-phenylisoquinoline-3,4-dicarboxylate (13)

Oxadiazoline **2e** (488 mg, 1.5 mmol) in benzene, heated with DMAD (745 mg, 5.25 mmol) and worked up as described previously, gave 85 mg (2.7 mmol, 18%) of **13**.[4]

White solid, mp 126 to 127 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 4.03 (s, 3H), 4.12 (s, 3H), 7.52–7.56 (m, 3H), 7.68–7.71 (m, 3H), 7.83 (t, J = 7.5 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 53.3, 53.4, 125.7, 127.6, 127.8, 128.3, 128.7, 129.5, 129.8, 130.3, 131.8, 132.2, 133.8, 138.5, 162.3, 166.1, 168.2. The structure of **13** was determined by means of X-ray crystallography.

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[4] Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3655. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 264346 contains the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).