Chemistry of cyclic aminooxycarbenes

Philippe Couture and John Warkentin

Abstract: A series of oxazolidin-2-ylidenes and one tetrahydro-1,3-oxazin-2-ylidene, generated by thermolysis of Δ^3-1,3,4-oxadiazolines in benzene at 90°C, were intercepted by insertion into the OH bond of phenols. In two cases the initial products rearranged to *N*-(2-aryloxyethyl)-*N*-methylformamides. The activation energy for rotation about the amide CN bond of those ultimate products was measured as 20.4 kcal/mol. The aminooxycarbenes reacted with two equivalents of methyl or phenyl isocyanate to give spiro-fused hydantoins. Major products from the reactions of the *N*-carbonyl carbenes with dimethyl acetylenedicarboxylate or with methyl propiolate were 2-oxazolines resulting from apparent acyl transfers from N to C in the proposed dipolar intermediates; minor products of 1:2 (carbene:trap) stoichiometry were also observed.

Key words: nucleophilic carbene, aminooxycarbene, oxadiazoline, amide rotation, oxazolidine.

Résumé : Une série d'oxazolidin-2-ylidènes et un tétrahydro-1,3-oxazin-2-ylidène, générés par thermolyse de Δ^3-1,3,4-oxadiazolines dans le benzène à 90°C, ont pu être interceptés par insertion dans la liaison OH de phénols. Dans deux cas, les produits initiaux se transposent en *N*-(2-aryloxyéthyl)-*N*-méthylformamides. On a établi que l'énergie autour de la liaison C—N de l'amide des produits ultimes est égale à 20,4 kcal/mol. Les aminooxycarbènes réagissent avec deux équivalents d'isocyanate de méthyle ou de phényle pour donner des hydantoïnes à jonction spiro. Les produits principaux des réactions des *N*-carbonylcarbènes avec l'acétylènedicarboxylate de diméthyle ou avec le propiolate de méthyle sont des 2-oxazolines provenant de transferts apparents d'acyle du N au C dans les intermédiaires dipolaires suggérés; on a aussi observé la présence de produits mineurs de stoechiométrie 1 : 2 (carbène : piège).

Mots clés : carbène nucléophile, aminooxycarbène, oxadiazoline, rotation d'amide, oxazolidine.

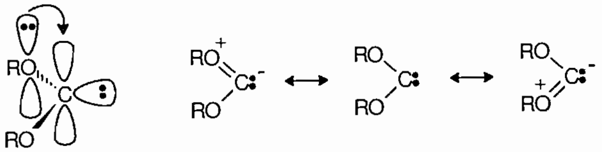
[Traduit par la rédaction]

Introduction

The driving force behind carbene reactions, in general, is the completion of the octet of electrons at the electron-deficient carbon. It is therefore expected that carbenes should behave as electrophiles, and react more rapidly with electron-rich substrates than with electron-deficient ones. Indeed, relative reactivity measurements carried out by Skell and Garner (1) and Doering and Henderson (2) in the late 1950s demonstrated such electrophilic natures for both CBr_2 and CCl_2. Since then, however, the selection of carbenes available has grown tremendously, and "philicity" in singlet carbenes now extends from the traditional electrophiles to the more unconventional ambiphiles and nucleophiles (3).

The intrinsic need to acquire a completed valence shell is not as strong in carbenes bearing one or two π-donor substituents on the carbene centre. Conjugative donation to the formally vacant carbenic *p*-orbital by heteroatoms such as N and O stabilizes the singlet state substantially and gives the carbene dipolar character (Fig. 1). Such carbenes react as nucleophiles or ambiphiles (3*b*). Dimethoxycarbene, the archetypal nucleophilic carbene, is generally unreactive towards electron-rich alkenes, but it adds readily to chloroacrylonitrile (4) and other electron-deficient alkenes (5).

Fig. 1.



Carbene reactivity thus spans an enormous range. For instance, whereas simple alkylcarbenes are notoriously difficult to study because of rapid intramolecular reactions (6), methoxymethylcarbene undergoes intermolecular cycloaddition reactions with a variety of alkenes (7). Dialkoxycarbenes do not react with toluene or benzene by either cyclopropanation or by C—H insertion, but dimerize in such solvents (8). This stabilization of singlet carbenes by substituents reaches an extreme in the case of the stable diaminocarbenes first isolated by Arduengo et al. (9).

Carbenes in which the two substituents are aza, oxa, or thia groups, or any permutations of such groups, are carbonyl group equivalents and, as such, they have considerable synthetic potential. One strategy for optimizing their utility involves the tuning of their reactivity by using different combinations of OR, NRR′, and SR as carbene substituents. The aza substituent is the most versatile because of the two variable moieties R and R′. In this paper, we present some results on the intermolecular reactivity of carbenes possessing the combination of OR and NRR′ substituents.[2] Aminooxycarbenes have only rarely been reported (10), and little is there-

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P. Couture and J. Warkentin.[1] Department of Chemistry, McMaster University, Hamilton, ON L8S 4M1, Canada.

[1] Author to whom correspondence may be addressed. Telephone: (905) 525-9140. Fax: (905) 522-2509. E-mail: Warkent@McMaster.ca

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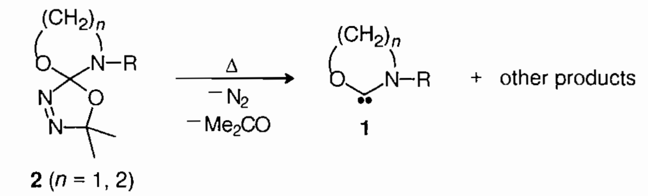
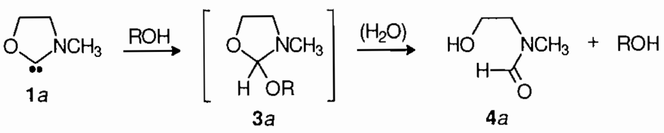
[2] A preliminary report on some of this work has been published (10*q*).

Scheme 1.



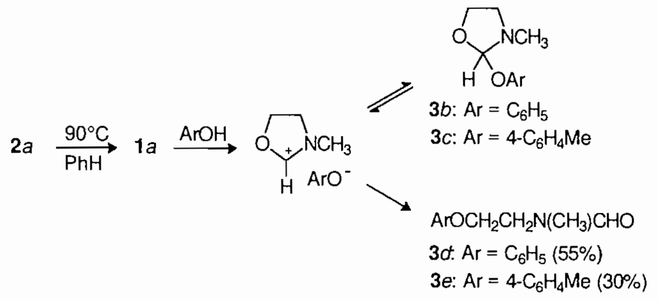
a: $n = 2$, R = Me; *b*: $n = 2$, R = C(O)H; *c*: $n = 2$, R = C(O)Me; *d*: $n = 2$, R = C(O)C(Me)=CH_2; *e*: $n = 2$, R = C(O)Ph; *f*: $n = 2$, R = C(O)OMe; *g*: $n = 2$, R = SO_2Ph; *h*: $n = 3$, R = C(O)Ph.

Scheme 2.



R = tBu, $PhCH_2$

Scheme 3.



fore known about their properties. In particular, we demonstrate herein that fragmentation of 5-membered aminooxycarbenes **1** ($n = 2$) to ethylene and an isocyanate (11) is sufficiently slow to allow the carbenes to participate in bimolecular reactions with a variety of substrates, in contrast to the dioxy (10*d*, 12) and dithio (13) analogues.

Methods, results, and discussion

Aminooxycarbenes **1** were generated by thermolysis of Δ^3-1,3,4-oxadiazolines (**2**) in benzene solutions at 90°C (Scheme 1). Details of the syntheses and thermolyses of the oxadiazolines **2** have been described in the preceding paper (11) and **2***a* was also reported recently by Rigby's group (10*p*).

Insertions into OH bonds

The reaction of nucleophilic carbenes with hydroxyl compounds results in the net insertion of the carbene into the O—H bond (14). In fact, the formation of such adducts is often regarded as evidence for the intermediacy of carbenes. Trapping of carbene **1***a* was first attempted by thermolysing the precursor oxadiazoline, **2***a*, in the presence of *tert*-butyl alcohol. Instead of the expected product (**3***a*), ^{1}H NMR and GC–MS analyses of the thermolysate revealed *N*-(2-hydroxyethyl)-*N*-methylformamide (**4***a*) to be the major alcohol-derived product.[3] The same product was obtained in the thermolysis of **2***a* in the presence of benzyl alcohol.[4] These results may be explained in terms of the facile hydrolysis of the 2-oxy oxazolidines **3***a* upon exposure to the atmosphere (Scheme 2).

Table 1. Selected NMR data[a] for *N*-(2-aryloxyethyl)-*N*-methylformamides **3***d*, *e*.

		3*d* (~53:47)	**3***e* (~54:46)
^{1}H NMR	NCH_3	**2.96** (s), 3.12 (s)	**2.95** (s), 3.10 (s)
	NCH_2	**3.62** (t), 3.73 (t)	**3.60** (t), 3.71 (t)
	OCH_2	**4.07** (t), 4.14 (t)	**4.03** (t), 4.10 (t)
	CHO	8.08 (s), **8.14** (s)	8.07 (s), **8.13** (s)
^{13}C NMR	NCH_3	30.24, **36.42**	30.18, **36.35**
	NCH_2	44.29, **49.04**	44.28, **49.04**
	OCH_2	**64.90**, 66.17	**65.11**, 66.34
	CHO	162.86, **163.25**	162.82, **163.23**

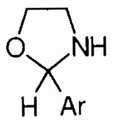
[a] Reported in ppm, in $CDCl_3$. Resonances from major conformers, assigned from the relative intensities of signals, are in bold, with the relative populations indicated in parentheses in the heading.

Like **3***a*, 2-aryloxyoxazolidines **3***b* and **3***c*, expected from the trapping of **1***a* with phenol and *p*-cresol, respectively, were not stable enough to survive the reaction conditions. The actual products, **3***e* and **3***d*, were again those of ring opening, presumably by reversible ion pair formation and eventual substitution by phenoxide at the OCH_2 group (Scheme 3).[5]

To confirm that the isolated products were formamides and not the novel oxazolidines **3***b* and **3***c*, NMR spectra were acquired at different temperatures to estimate the barrier, either to pyramidal inversion at nitrogen for the cases of **3***b*, *c* or to amide rotation for the cases of **3***d*, *e*. At room temperature, two sets of well-resolved signals of almost equal intensity, each one corresponding to one conformer, were observed in both the ^{1}H and ^{13}C spectra; selected NMR data are shown in Table 1.[6]

The nearly equal conformer populations allowed us to estimate the magnitude of the barrier by means of the coalescence method (15). Figure 2 shows the ^{1}H spectrum of **3***e* as a function of temperature, where coalescence of the N-methyl singlets was observed at ca. 135°C. Within experimental error, identical barriers of 20.4 kcal/mol were found for **3***d* and **3***e*.

Although high inversion barriers are common in small N-heterocycles such as aziridines (16), to our knowledge only



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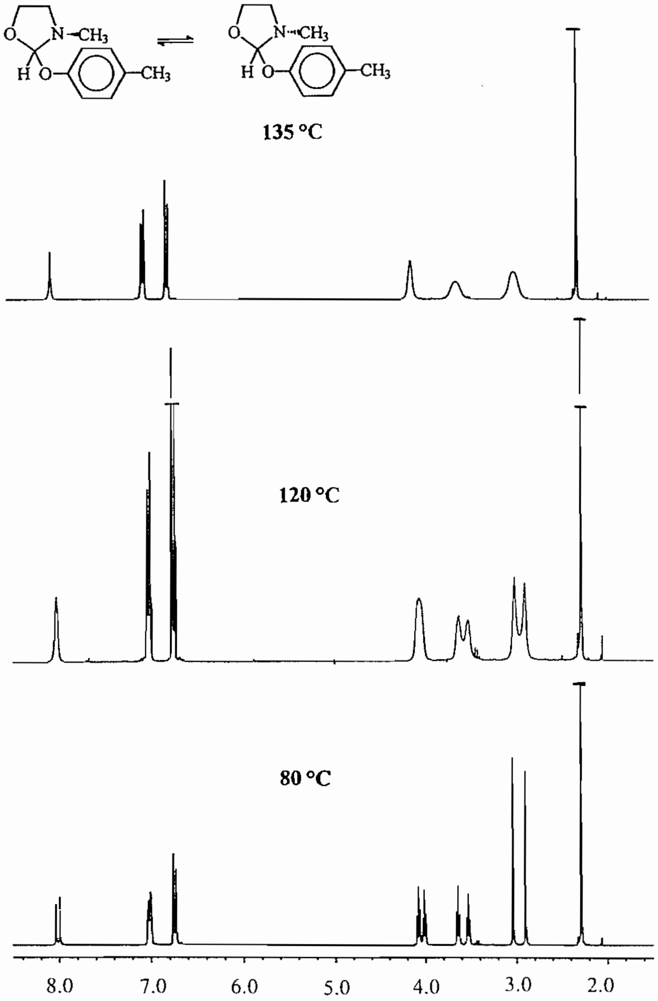
[3] The identity of **4***a* was confirmed by comparison with an authentic sample.

[4] A small amount of benzyl formate was also observed, suggesting the occurrence of a competing hydrolysis mechanism.

[5] The lower yield of **3***d* is attributed to some loss of material during purification.

[6] Peak assignments were confirmed by means of double-irradiation experiments; for instance, the OCH_2 triplet at 4.07 ppm in **3***d* is coupled to the NCH_2 triplet at 3.62 ppm.

Fig. 2. 300 MHz ^{1}H spectrum of **3***c*, in hexachloro-1,3-butadiene, as a function of temperature. Spectra at 110, 130, and 140°C were also taken.



one report of such high barriers involving oxazolidines appears in the literature. Yang et al. (17) reported $\Delta G^{\ddagger}$ values of 20.7–22.3 kcal/mol for N-inversion in a series of 2-aryloxazolidines **5** unsubstituted at N. The much lower barriers in other known oxazolidines,[7] and the fact that amide rotation is associated with a barrier of ca. 20 kcal/mol, suggested that our products were amides. The ^{1}H and ^{13}C spectra (Table 1) are in agreement with the formamide assignments, **3***d*, *e*. In particular, the signal at 163 ppm would have to be assigned to C2, and that at 8.1 ppm to the proton at C2 of **3***b*, *c* if those structures were applicable. Oxazolidines with a heteroatom substituent at C2 are relatively rare, and they usually bear an electron-withdrawing group on N. In these compounds, the C2 signal typically appears near 112 ppm (ca. 50 ppm to higher field), as shown in Fig. 3 for two 2-alkoxyoxazolidines and some related compounds (18–20). Similarly, the C2 signal of 2-aryloxyoxazolidines bearing a carbonyl group on N appears near 105 ppm, and the C2-H is observed at 6.0–6.7 ppm (see **3***f*–*m* below). If oxazolidines **3***b*, *c* were applicable structures, they would have to exist as ion pairs in chloroform solution in order to match observed spectral characteristics. Models for both an undissociated oxazolidine (**6**) and the corresponding cation resulting from the loss of MeO^{-} (Fig. 4) were reported by Scholastico and co-workers (21).

N-Carbonyl oxadiazolines **2***b*–*f*, *h* fragmented to the corresponding aminooxycarbenes **1***b*–*f*, *h* (11) in high yields, as indicated by the results of trapping with phenols (Scheme 4, Table 2). *N*-Carbonyl adducts **3***f*–*m* were sensitive to hydrolysis and they could not be purified by chromatography. Compound **3***j* crystallized by addition of a mixture of ethyl acetate and hexane to the crude oil. Unfortunately, this procedure failed to produce crystals in most other cases. However, essentially pure products could be obtained in high yields by simply base-washing the thermolysates in order to remove the excess phenol; the benzene solutions were then dried over $MgSO_4$, and the solvent and volatile products were evaporated in vacuo to afford products **3**.

The ^{1}H and ^{13}C NMR spectra of compounds **3***f*–*m*, which were briefly discussed above, usually showed broad resonances and (or) more than one set of peaks due to restricted rotation about the amide CN bond. Low-intensity molecular ions in the mass spectra were generally observed, in addition to the characteristic M − OAr cations.

Hydrolysis of a sample of **3***j* kept in $CDCl_3$ cleanly produced *N*-[2-(formyloxy)ethyl]benzamide (**7***a*) and phenol over the course of a few weeks, as shown in Scheme 5.[8] Tetrahydro-1,3-oxazine **3***m* was more labile and partial hydrolysis was observable immediately after dissolving it in $CDCl_3$. In this solvent, **7***b* and phenol were the only products (Scheme 5). In contrast, the major fraction collected during an attempt to purify **3***m* by chromatography on silica consisted of a mixture of two related products, **7***b* and a material tentatively identified as **4***b*. Periodic recording of the ^{1}H NMR spectrum of this mixture, kept in $CDCl_3$, showed the gradual conversion of **4***b* into **7***b*, which was complete within 1 month (Scheme 5).

Thermolysis of **2***g* in the presence of phenol led to the formation of several products (11), but the anticipated carbene insertion product, **3***n*, could not be unambiguously identified. However, formamide **4***c*, probably derived from hydrolysis of **3***n*, was isolated (Scheme 6).

Reactions with isocyanates

Nucleophilic carbenes have been reported to react with alkyl or aryl isocyanates to give hydantoins (**8**) as final products (8, 10*k*, 22). Their formation was explained in terms of an initial attack of the carbene on the carbonyl carbon of the isocyanate, followed by 1,3-dipolar cycloaddition of the intermediate across the C=N bond of a second molecule of isocyanate (Scheme 7).[9] As anticipated, the generation of aminooxycarbenes **1** in the presence of methyl or phenyl isocyanate led to the isolation of the corresponding spiro-fused hydantoins **8***a*–*f* (Scheme 8, Table 3).

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[7] For examples of related oxazolidines, see ref. (18).

[8] Sample was kept in the refrigerator for about 2 months and it was not examined regularly.

[9] These reactions contrast with the [1 + 4] cycloadditions between nucleophilic carbenes and benzoyl isocyanate, which yield 4(5*H*)-oxazolones (11).

Fig. 3. Selected NMR data for some models for 3*b*, *c*.

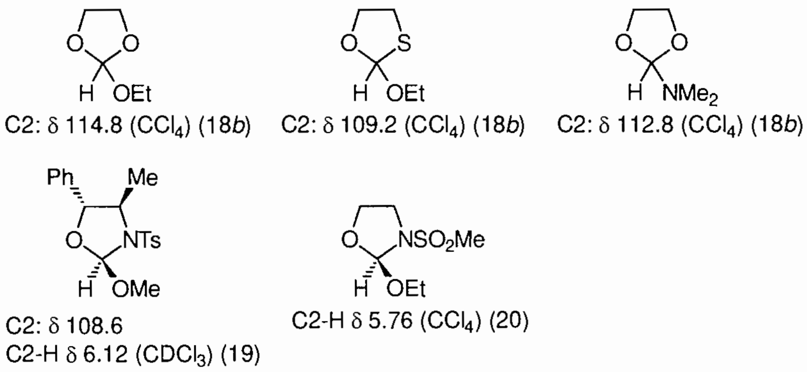
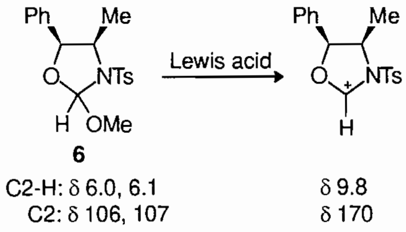
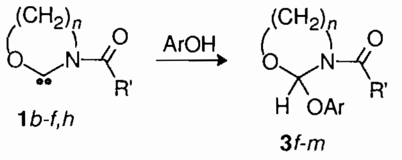


Fig. 4. Selected NMR data for **6** and the corresponding oxazolidinium cation (21).



Scheme 4.



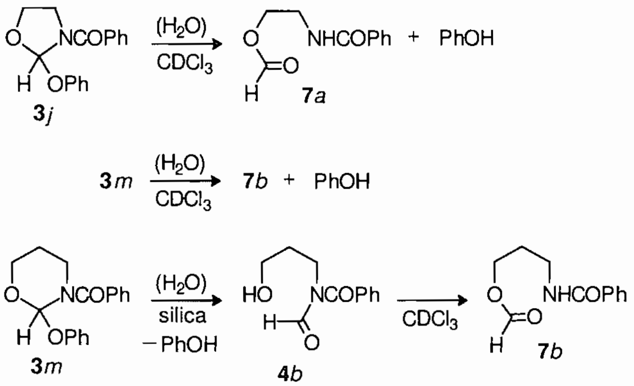
Reactions with alkynes

The reactivity of aminooxycarbenes **1** towards activated alkynes was also examined. Thermolysis of oxadiazoline **2***e* with 2.1 equivalents of dimethyl acetylenedicarboxylate (DMAD) gave three products, derived from reactions of carbene **1***e* with DMAD, that were isolated by chromatography, Scheme 9. The major product, oxazoline **9***a*, obtained in 73% yield, was apparently formed via benzoyl group transfer from N to C in the presumed 1,3-dipolar intermediate **10** (10*q*). That rearrangement is analogous to an aryl group transfer reported by Scherowsky's group (23). One of the minor products was assigned structure **11***a* (one of two possible diastereomers), by comparison of its spectral data with those of analogous dihydrofurans formed in the reaction of DMAD with other nucleophilic carbenes (5, 24). Its formation is rationalized in terms of the mechanism proposed by Hoffmann et al. (5) for the reaction of dimethoxycarbene with DMAD, where the dipolar intermediate (**10**, in the present case), formed by attack of the carbene at a triple-bonded carbon, adds across the carbonyl group of a second molecule of the alkyne (Scheme 9). For the third product, all spectral data were consistent with a 1:2 stoichiometry (carbene:DMAD), but its structure could not be elucidated.[10]

Table 2. *N*-Carbonyl carbene–phenol adducts (**3**) isolated.

	n	R′	Ar	Yield (%)
3*f*	2	H	Ph	75
3*g*	2	Me	Ph	89
3*h*	2	C(Me)=CH$_2$	Ph	97
3*i*	2	C(Me)=CH$_2$	4-C$_6$H$_4$CN	84
3*j*	2	Ph	Ph	76
3*k*	2	Ph	4-C$_6$H$_4$CN	90
3*l*	2	OMe	Ph	>90
3*m*	3	Ph	Ph	97

Scheme 5.



2-Oxazolines bearing a substituent at C2 can be cleaved by hydrolysis or alcoholysis to the corresponding carboxylic acids or esters, respectively (25). As shown in Scheme 10, treatment of **9***a* with acetic acid in methanol gave a mixture of two inseparable compounds, namely, the expected triester **12** and an isomer tentatively assigned structure **13***a* (isomer **13***b* was ruled out (26)). Dihydrofuran derivative **13***a* likely results from the acid-catalyzed rearrangement of **12**.

In view of the reaction of **1***e* with DMAD, it was of interest to see if the same carbene would react with the less electrophilic methyl propiolate. From ^{1}H NMR analysis of the crude product after thermolysis, oxazoline **14** was clearly the major product (Scheme 11). However, substantial decomposition occurred during two successive separations by chromatography, and **14** was isolated in only 4% yield.

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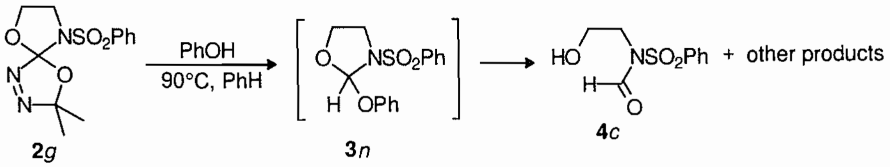
[10] Not the diastereo isomer of **11***a*.

Table 3. Hydantoins **8** isolated from reactions of **1** with methyl or phenyl isocyanate.

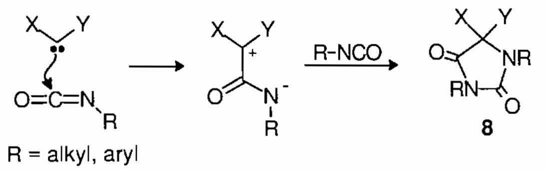
	n	R	R′	Yield (%)
8*a*	2	Me	Me	44
8*b*	2	Me	Ph	27
8*c*	2	C(O)Me	Ph	87
8*d*	2	C(O)C(Me)=CH_2	Ph	72
8*e*	2	C(O)Ph	Ph	76
8*f*	3	C(O)Ph	Me	78

Scheme 6.



2*g* 3*n* 4*c*

Scheme 7.



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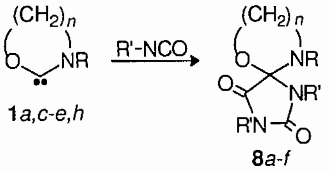
Scheme 8.



1*a,c-e,h* 8*a-f*

Reactions of aminooxycarbenes **1***c* (*N*-acetyl) and **1***d* (*N*-methacryloyl) with DMAD were also investigated and, in both cases, carbonyl group transfers were observed. Thus, thermolysis of oxadiazoline **2***d* with an excess of the alkyne afforded oxazoline **9***b*, isolated in 54% yield, as the major product (Scheme 12).

Thermolysis of **2***c* under similar conditions produced at least five different 1:2 adducts (carbene:DMAD), in addition to oxazoline **9***c*, as shown in Scheme 13. The latter, which appeared to be a major product from analysis of the crude thermolysate, decomposed completely during attempted separation by chromatography. This procedure, however, was successful in separating the 1:2 adducts from one another. Two of them were identified as the pair of diastereomers **11***b* and **11***c*, the latter (see experimental) being the analogue of **11***a*. Of the remaining three low-yield adducts, one was the analogue of the unidentified product reported above in the reaction of **1***e* with DMAD (Scheme 9).

Thermolysis of *N*-sulfonyl oxadiazoline **2***g* in the presence of DMAD also led to the isolation of several products, Scheme 14. Among them was oxazolidinone **15**, produced in a thermolytic fragmentation that competes with carbene generation (11). 2-Diazopropane, the coproduct of **15**, reacted with DMAD to give pyrazole **16** (11, 27). The only carbene + DMAD adduct that could be unambiguously identified was spiro-fused cyclopentadiene **17**, which apparently results from the unusual addition of the dipolar intermediate (the analogue of **10**) across the triple bond of a second molecule of DMAD.[11] Finally, compound **18** was also isolated in low yield; its origin is not known at present.

Experimental

General methods

Radial chromatography was performed with a Chromatotron apparatus, model 7924T (Harrison Research Inc.), with silica-coated plates of 1 mm, 2 mm, or 4 mm thickness. NMR spectra were recorded on a Bruker AC-200 or AC-300 spectrometer; signals labelled "um" appear as broad unresolved multiplets because of slow exchange. Infrared spectra were recorded with a Biorad FTS-40 spectrophotometer, with the sample either in CCl_4 or in KBr as a pellet. The IR bands are labelled qualitatively with the symbols br for broad, app for apparent, and s, m, and w for strong, medium, and weak intensities, respectively. Bands from C–H stretching vibrations between 2850 and 3100 cm^{-1} are omitted, as are very weak bands. Mass spectra were obtained on a VG Analytical ZAB-E double focusing mass spectrometer or on a HP-5890 Series II gas chromatograph with a 5971A mass selective detector. Melting points were recorded on a Thomas Hoover capillary melting point apparatus, and are reported uncorrected. Elemental analyses were performed by Guelph Chemical Laboratories, Ltd. (Guelph, Ontario).

General methods for thermolyses

Benzene used as a thermolysis solvent was distilled from sodium benzophenone, and stored over molecular sieves.

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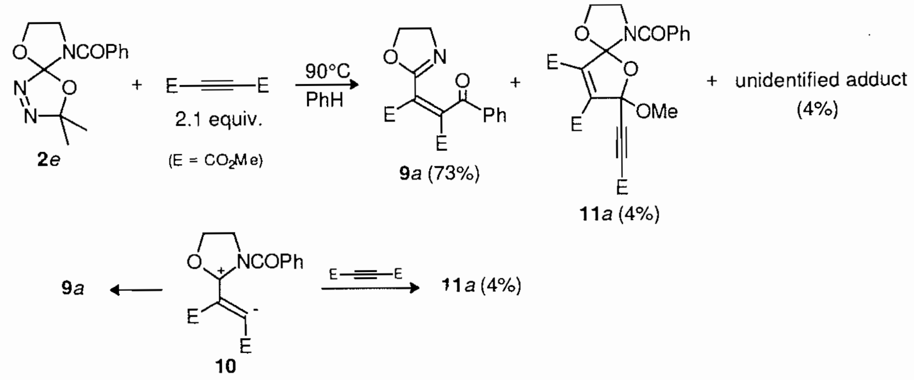
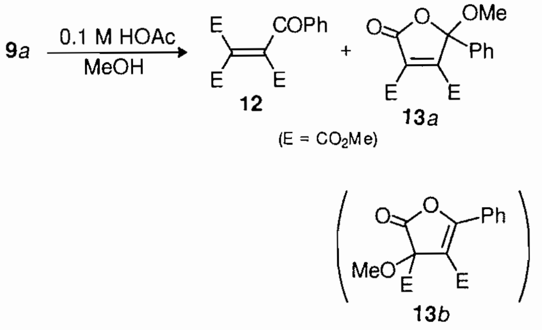
[11] The more commonly observed adducts of type **11** were probably formed but they could not be identified with certainty, due to difficulties in the separation. In addition, a 1:3 adduct (carbene:DMAD) was isolated, but its low yield (ca. 1%) prevented a definite structural assignment.

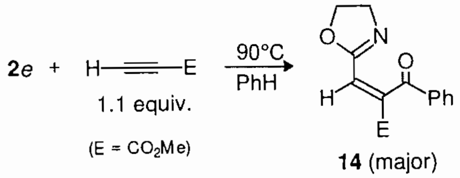
Scheme 9.



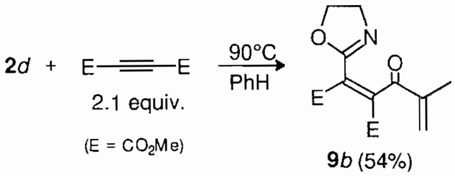
Scheme 10.



Scheme 11.



Scheme 12.



Typically, a benzene solution (10 mL) of the oxadiazoline[12] (0.5 mmol, 50 mM) and a specified amount of compound used as carbene trap were transferred to a sealable thermolysis tube. In some cases, this was preceded by distilling, under a dry nitrogen atmosphere, approximately 20 mL of the solution to be thermolysed down to 10 mL, in order to azeotrope out any water. The tube was then evacuated, sealed, and immersed in a constant temperature oil bath at 90°C ± 0.2°C for 24 h unless otherwise stated. The solvent and volatile products were removed with a rotary evaporator prior to analysis of the crude thermolysate by NMR and, in some cases, GC–MS. Thermolysis products were then separated and purified as described below.

Reactions with alcohols

Thermolysis of 2a *with* tert-*butyl alcohol*

Oxadiazoline **2***a* (15 mg, 0.085 mmol) was heated with *tert*-butyl alcohol (40 μL, 0.42 mmol, dried by refluxing over calcium hydride followed by distillation) in a sealed NMR tube in ca. 0.5 mL of benzene-d_6. Analysis of the crude thermolysate by ^{1}H NMR and GC–MS revealed the presence of **4***a*.

N-*(2-Hydroxyethyl)*-N-*methylformamide (4*a*)*: An authentic sample was prepared from the reaction of 2-(methylamino)-1-ethanol with ethyl formate, as described by Shibanuma et al. (28). Colourless oil; ^{1}H NMR (300 MHz, CDCl$_3$, slow exchange, signals due to major isomer are underlined, A:B ≈ 60:40) δ: 2.87 (s) and 3.02 (s) (3H, NCH$_3$), 3.24–3.85 (m) and 4.25–4.35 (m) (5H, CH$_2$CH$_2$, OH), 8.00 (s) and 8.05 (s) (1H, C(O)H); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 29.78 and 35.81 (NCH$_3$), 47.54 and 52.13 (NCH$_2$), 58.62 and 60.11 (OCH$_2$), 163.56 and 163.78 (C═O); MS (EI) *m/z*: 103 (M$^+$, 2), 85 (5), 72 (19), 60 (11), 56 (8), 44 (100), 29 (45).

Thermolysis of 2a *with benzyl alcohol*

Oxadiazoline **2***a* (103 mg, 0.60 mmol) was heated with benzyl alcohol (99 mg, 0.91 mmol) in 10 mL of benzene. Formamide **4***a* (above) was the major aminooxycarbene-derived product (by ^{1}H NMR and GC–MS); a small amount of benzyl formate was also observed.

Benzyl formate (ref. 29): MS (EI) *m/z*: 136 (M$^+$, 27), 108 (37), 91 (100), 77 (75), 65 (37), 51 (43), 39 (26), 29 (49).

Reactions of carbene 1*a* with phenols

N-*Methyl*-N-*(2-phenoxyethyl)fomamide (3*d*)*

Oxadiazoline **2***a* (84 mg, 0.49 mmol) was heated with phenol (58 mg, 0.62 mmol) in 10 mL of benzene. Purification by radial chromatography, with 10–60% ethyl acetate in hexane, gave **3***d* in 55% yield. Colourless oil; IR (CCl$_4$) cm^{-1}: 1771m, 1684s, 1600m, 1497s, 1382m, 1301w, 1242s, 1173w, 1081m,

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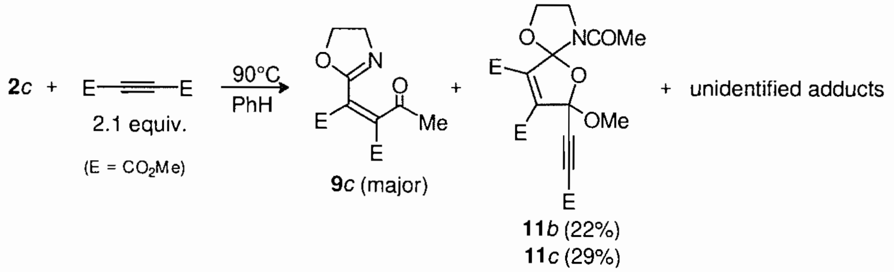
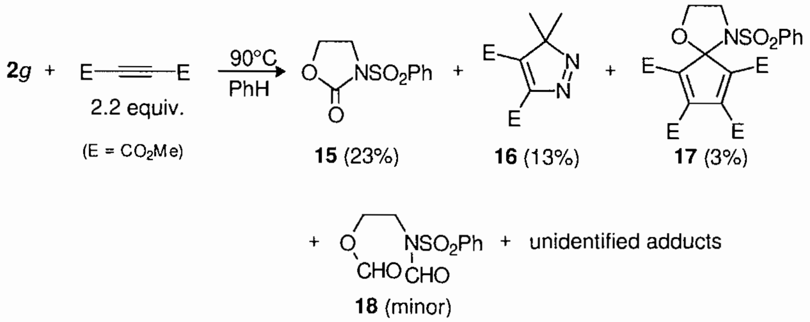
[12] Details of the syntheses of oxadiazolines **2** have been described (11).

Scheme 13.



Scheme 14.



1056m, 908w; ^{1}H NMR (300 MHz, CDCl$_3$, slow rotation, signals from the major rotamer are underlined, A:B ≈ 53:47) δ: 2.96 (s) and 3.12 (s) (3H, NCH$_3$), 3.62 (t, ^3J = 5.2 Hz) and 3.73 (t, ^3J = 5.2 Hz) (2H, NCH$_2$), 4.07 (t, ^3J = 5.2 Hz) & 4.14 (t, ^3J = 5.2 Hz) (2H, OCH$_2$), 6.84–7.02 (m, 3H, Ar-*o,p*), 7.23–7.33 (m, 2H, Ar-*m*), 8.08 (s) and 8.14 (s) (1H, CHO); ^{13}C NMR (75 MHz, CDCl$_3$) δ: 30.24 and 36.42 (NCH$_3$), 44.29 and 49.04 (NCH$_2$), 64.90 and 66.17 (OCH$_2$), 114.42 and 114.56 (OPh C2, C6), 121.14 and 121.46 (OPh C4), 129.59 (OPh C3, C5), 158.13 and 158.41 (OPh C1), 162.86 and 163.25 (CHO); MS (EI) *m*/*z*: 179 (M$^+$, 1), 149 (1), 120 (14), 107 (6), 91 (19), 86 (M-OPh, 100), 77 (81), 72 (21), 65 (42), 58 (84), 51 (45), 44 (81), 39 (47), 28 (36); MS (CI, NH$_3$) *m*/*z*: 197 (M + NH$_4$)$^+$, 180 (M + H)$^+$.

N-*Methyl*-N-*(2-(4-methylphenoxy)ethyl)formamide (3*e*)*

Oxadiazoline 2*a* (90 mg, 0.52 mmol) was heated with *p*-cresol (93 mg, 0.86 mmol) in 10 mL of benzene. Purification by radial chromatography, with 20–40% ethyl acetate in hexane, gave 3*e* in 30% yield. Colourless oil; ^{1}H NMR (200 MHz, CDCl$_3$, slow rotation, signals from the major rotamer are underlined, A : B ≈ 54 : 46) δ: 2.28 (s, 3H, Ar-CH$_3$), 2.95 (s) and 3.10 (s) (3H, NCH$_3$), 3.60 (t, ^3J = 5.2 Hz) and 3.71 (t, ^3J = 5.2 Hz) (2H, NCH$_2$), 4.03 (t, ^3J = 5.2 Hz) and 4.10 (t, ^3J = 5.2 Hz) (2H, OCH$_2$), 6.77 (app d, ^3J = 8.6 Hz, 2H, Ar C(2,6)H), 7.08 (app d, ^3J = 8.6 Hz, 2H, Ar C(3,5), 8.07 (s) and 8.13 (s) (1H, CHO); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 20.46 (Ar-CH$_3$), 30.18 and 36.35 (NCH$_3$), 44.28 and 49.04 (NCH$_2$), 65.11 and 66.34 (OCH$_2$), 114.29 and 114.45 (OAr C2, C6), 130.00 (OAr C3, C5), 130.34 and 130.72 (OAr C4), 156.06 and 156.31 (OAr C1), 162.82 and 163.23 (CHO); MS (EI) *m*/*z*: 193 (M$^+$, 1), 149 (1), 134 (5), 119 (7), 107 (15), 91 (40), 86 (M − OPh, 100), 77 (37), 65 (28), 58 (73), 51 (16), 44 (42), 28 (19).

Reactions of carbenes 1*b*–*g* with phenols

Compounds 3*f*–*n* are very easily hydrolysed and they could not be purified by chromatography. Products of reasonable purity were generally obtained after the following work-up: the excess phenol was removed by washing the thermolysate, diluted to 25 mL with fresh benzene, with 4 × 5 mL of aqueous NaOH (5%), followed by 5 mL of water or brine; this was followed by extraction of the combined aqueous layers with one portion of benzene, and drying of the organic phase over MgSO$_4$.

*3-Formyl-2-phenoxyoxazolidine (3*f*)*

Oxadiazoline 2*b* (49 mg, 0.26 mmol) was heated with phenol (39 mg, 0.41 mmol) in 10 mL of benzene. Work-up as indicated above gave 3f as a colourless oil in 75% yield. IR (CCl$_4$) cm^{-1}: 1699s (C═O), 1591m, 1494m, 1415m, 1385m, 1356m, 1297w, 1205s, 1117w, 1083m, 1030w, 1010m, 991m, 953w, 876w; ^{1}H NMR (200 MHz, C$_6$D$_6$, slow exchange) δ: ca. 2.4–3.9 (um's, 4H, OCH$_2$CH$_2$N), 6.03 (s) and 6.07 (s) (1H, C(2)H), 6.85–7.40 (m, 5H, Ar), 7.90 (br s) and 8.27 (br s) (1H, C(O)H); ^{13}C NMR (50 MHz, C$_6$D$_6$, slow exchange, signals from major isomer are underlined) δ: 41.12 and 42.09 (NCH$_2$), 64.61 (OCH$_2$), 102.91 and 104.34 (C2), 117.96 and 118.52 (OPh C2, C6), 123.18 (OPh C4), 129.79 (OPh C3, C5), 155.47 (OPh C1), 158.87 and 159.27 (C═O); MS (EI) *m*/*z*: 193 (M$^+$, 1), 134 (2), 107 (1), 100 (M − OPh, 100), 94 (27), 78 (8), 72 (68), 65 (28), 51 (7), 44 (72), 39 (31), 29 (15); MS (CI, NH$_3$) did not give useful information.

*3-Acetyl-2-phenoxyoxazolidine (3*g*)*

Oxadiazoline 2*c* (96 mg, 0.48 mmol) was heated with phenol (59 mg, 0.63 mmol) in 10 mL of benzene. The usual work-up gave 3*g* as an oil in 89% yield; all attempts to crystallize the oil failed. IR (CCl$_4$) cm^{-1}: 1735w, 1683s (C═O), 1594m, 1494m, 1406m, 1357m, 1210s, 1099w, 1061w, 1007m, 980m, 946m; ^{1}H NMR (200 MHz, CDCl$_3$, slow exchange) δ: 1.85 (s) and 2.15 (s) (3H, CH$_3$), 3.58–3.92 (m, 2H, NCH$_2$), 4.20–4.52 (m, 2H, OCH_2), 6.39 (s) and 6.66 (s) (1H, C(2)H), 7.06–7.17 (m, 3H, Ar-*o,p*), 7.25–7.40 (m, 2H, Ar-*m*); ^{13}C NMR (50 MHz, $CDCl_3$, slow exchange, signals from major isomer are underlined) δ: 22.41 and 22.79 (CH_3), 43.27 and 44.65 (NCH_2), 64.83 and 65.31 (OCH_2), 103.84 and 104.34 (C2), 117.52 and 118.21 (OPh C2, C6), 122.96 and 123.24 (OPh C4), 129.41 and 129.68 (OPh C3, C5), 154.93 and 155.45 (OPh C1), 168.12 and 168.43 (C=O); MS (EI) *m/z*: 207 (M^+, 2), 135 (3), 114 (M − OPh, 65), 94 (29), 84 (13), 72 (100), 65 (18), 49 (20), 44 (39); MS (CI, NH_3) *m/z*: 208 $(M + H)^+$.

*3-Methacryloyl-2-phenoxyoxazolidine (3*h*)*

Thermolysis of oxadiazoline **2***d* (71 mg, 0.32 mmol) in the presence of phenol (44 mg, 0.68 mmol) in 10 mL of benzene gave, after the usual work-up, **3***h* as a viscous, colourless oil in 97% yield. IR (CCl_4) cm^{-1}: 1734w, 1667s (C=O), 1632m, 1591w, 1496m, 1454w, 1396m, 1370m, 1200s, 1118w, 1084w, 1007m, 982s, 948m, 891; ^{1}H NMR (200 MHz, $CDCl_3$, slow exchange, some peaks are broad) δ: 2.00 (app t, ^4J = 1.3 Hz, 3H, CH_3), 3.75–3.87 (m, 2H, NCH_2), 4.20–4.44 (m, 2H, OCH_2), 5.31 (br s, 1H, $=CH_2$), 5.42 (app t, ^4J = 0.9 Hz, 1H, $=CH_2$), 6.51 (br s, 1H, C(2)H), 7.00–7.13 (m, 3H, Ar-*o,p*), 7.25–7.39 (m, 2H, Ar-*m*); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 19.98 (CH_3), 43.31 (NCH_2), 64.52 (OCH_2), 105.23 (C2), 117.62 and 117.82 (OPh C2, C6, and $=CH_2$), 123.02 (OPh C4), 129.85 (OPh C3, C5), 141.66 ($=CR_2$), 155.69 (OPh C1), 169.09 (C=O); MS (EI) did not give useful information; MS (CI, NH_3) *m/z*: 234 $(M + H)^+$.

*2-(4-Cyanophenoxy)-3-methacryloyloxazolidine (3*i*)*

Thermolysis of oxadiazoline **2***d* (100 mg, 0.44 mmol) in the presence of 4-cyanophenol (62 mg, 0.52 mmol) in 10 mL of benzene gave a partially crystalline oil (84% yield) after the usual work-up. ^{1}H NMR (200 MHz, C_6D_6, slow exchange) δ: 1.81 (s, 3H, CH_3), ca. 3.0–4.0 (um, 4H, NCH_2, OCH_2), 4.89 (br s, 1H, $=CH_2$), 5.11 (br s, 1H, CH_2), 6.14 (br s) and 6.38 (br s) (1H, C(2)H), 6.55–7.20 (um, 4H, Ar); ^{13}C NMR (50 MHz, C_6D_6) δ: 19.84 (CH_3), 43.47 (br, NCH_2), 65.11 (OCH_2), 104.69 (OAr C4), 106.62 (C2), 117.53 (OAr C2, C6), 118.12 ($=CH_2$), 122.66 (C≡N), 134.00 (OAr C3, C5), 141.31 ($=CR_2$), 158.35 (OAr C1), 169.06 (C=O); MS (EI) *m/z*: 140 (M − OAr, 35), 119 (6), 84 (5), 69 (methacryloyl cation, 100), 64 (4), 49 (10), 41 (72); MS (CI, NH_3) *m/z*: 276 $(M + NH_4)^+$, 259 $(M + H)^+$.

*3-Benzoyl-2-phenoxyoxazolidine (3*j*)*

Oxadiazoline **2***e* (105 mg, 0.40 mmol) was heated with phenol (72 mg, 0.77 mmol) in 10 mL of benzene. After removal of the solvent and volatile products on the rotary evaporator, **3***j* solidified upon addition of 20% ethyl acetate in hexane. Recrystallization from the same solvent mixture yielded a white solid, mp 89–91°C (76% yield). IR (KBr) cm^{-1}: 1660s (C=O), 1591s, 1493w, 1448w, 1399s, 1201m, 1168w, 1115w, 1084m, 951m, 933m, 887m, 791w, 770w, 725w; ^{1}H NMR (200 MHz, $CDCl_3$, slow exchange) δ: 3.70–4.10 (um, 2H, NCH_2), 4.10–4.45 (um, 2H, OCH_2), 6.21 (br s, 1H, C(2)H), 6.70–7.10 (um, 3H, Ar), 7.10–7.45 (um, 5H, Ar), 7.55–7.65 (m, 2H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 43.48 (NCH_2), 64.60 (OCH_2), 105.19 (C2), 117.79 (OPh C2, C6), 123.12 (OPh C4), 127.58 (benzoyl C2, C6), 128.42 (benzoyl C3, C5), 129.52 (OPh C3, C5), 130.92 (benzoyl C4), 135.45 (benzoyl C1), 154.67 (OPh C1), 169.00 (C=O); MS (EI) *m/z*: 269 (M^+, 2), 198 (2), 176 (M − OPh, 14), 147 (18), 117 (20), 105 ($PhCO^+$, 100), 94 (21), 84 (42), 77 (42), 49 (54); MS (CI, NH_3) *m/z*: 270 $(M+H)^+$; HRMS calcd. for $C_{10}H_{10}NO_2$ (M − OPh): *m/z* 176.0712, found: *m/z* 176.0705.

*2-(4-Cyanophenoxy)-3-benzoyloxazolidine (3*k*)*

Oxadiazoline **2***e* (107 mg, 0.41 mmol) was thermolysed with 4-cyanophenol (59 mg, 0.49 mmol) in 10 mL of benzene. The usual work-up gave **3***k* as a white solid in 90% yield. IR (CCl_4) cm^{-1}: 2230m (C≡N), 1751s, 1672s (C=O), 1605s, 1507m, 1451w, 1384s, 1257m, 1210s, 1172m, 1080m, 1056m, 1022w, 962s, 889w, 836w; ^{1}H NMR (200 MHz, $CDCl_3$, slow exchange) δ: ca. 3–4 (um, 4H, NCH_2, OCH_2), ca. 5.8–8.3 (um, 10H, C(2)H, Ar); ^{13}C NMR (50 MHz, C_6D_6) δ: 44.06 (br, NCH_2), 65.10 (OCH_2), 104.96 (OAr C4), 106.74 (C2), 117.57 (OAr C2, C6), 122.74 (C≡N), ca. 128 (overlapped with solvent triplet, aroyl C2, C6 and C3, C5), 131.04 (aroyl C4), 135.83 (aroyl C1), 133.88 (OAr C3, C5), 158.19 (OAr C1), 168.6 (C=O); MS (EI) *m/z*: 176 (M − OAr, 38), 105 ($PhCO^+$, 100), 90 (6), 77 (32), 51 (10); MS (CI, NH_3) *m/z*: 295 $(M+H)^+$.

*3-Methoxycarbonyl-2-phenoxyoxazolidine (3*l*)*

Oxadiazoline **2***f* (55 mg, 0.26 mmol) was heated with phenol (30 mg, 0.32 mmol) in 10 mL of benzene. The usual work-up gave **3***l* as a colourless oil in quantitative yield. IR (CCl_4) cm^{-1}: 1728s (C=O), 1593m, 1494m, 1451s, 1391s, 1301w, 1212s, 1137w, 1076m, 987s, 692; ^{1}H NMR (200 MHz, C_6D_6, slow exchange) δ: ca. 2.9–4.1 (um's, 7H, OCH_2CH_2N, CH_3), 6.46 (br s) and 6.74 (br s) (1H, C(2)H), ca. 6.8–7.4 (um, 5H, Ar); ^{13}C NMR (50 MHz, C_6D_6, slow exchange) δ: 43.83 (NCH_2), 52.42 (CH_3), 64.73 and 65.14 (OCH_2), 104.52 and 105.52 (C2), 118.18 (OPh C2, C6), 122.97 (OPh C4), 129.79 (OPh C3, C5), 153.38 and 156.35 (OPh C1 and C=O); MS (EI) *m/z*: 223 (M^+, <1), 192 (2), 130 (M − OPh, 100), 94 (8), 78 (5), 70 (5), 65 (17), 58 (35), 39 (16), 30 (8); MS (CI, NH_3) did not give useful information.

*3-Benzoyl-2-phenoxytetrahydro-2*H*-1,3-oxazine (3*m*)*

Oxadiazoline **2***h* (100 mg, 0.36 mmol) was heated with phenol (52 mg, 0.55 mmol) in 10 mL of benzene. The usual work-up gave essentially pure **3***m* (97% yield), which crystallized upon addition of 10% ethyl acetate in hexane. White solid, mp ca. 83–92°C; IR (CCl_4) cm^{-1}: 1732w, 1663s (C=O), 1597m, 1496m, 1448w, 1416m, 1381m, 1356w, 1333w, 1287m, 1218m, 1196m, 1173m, 1090m, 1017m, 977s, 930m, 903w, 853w; ^{1}H NMR (300 MHz, C_6D_6, slow exchange) δ: 0.86–1.12 (um, 1H, CCH_2C), 1.63–1.85 (um, 1H, CCH_2C), 3.34–3.53 (um, 2H, NCH_2), 3.81–4.00 (um, 1H, OCH_2), 4.16–4.35 (um, 1H, OCH_2),[13] 6.80–7.25 (um, 9H) and 7.40–7.65 (um, 2H) (Ar and C(2)H); ^{13}C NMR (75 MHz, C_6D_6, slow exchange) δ: 24.28 (CCH_2C), 37.97 (NCH_2),[14] 59.49 (OCH_2), 99.66 (C2),[15] 117.26 (OPh C2, C6), 122.74 (OPh C4), ca. 127.5 (benzoyl C2, C6, under solvent triplet), 128.57 (benzoyl

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[13] One of the OCH_2 proton signals disappears at room temperature; at 90%C, it appears at 4.16–4.35 (um).

[14] At room temperature, the NCH_2 signal appears as a very wide resonance in the range 35–40 ppm; at 77°C, it is a slightly broadened singlet at 37.97 ppm.

[15] Taken at 77°C; at room temperature, the signal is broad, in the range 97–102 ppm.

C3, C5), 129.85 (OPh C3, C5), 130.21 (benzoyl C4), 135.68 (benzoyl C1), 155.58 (OPh C1), 169.36 (C═O); MS (EI) *m/z*: 266 (2), 190 (M − OPh, 66), 172 (4), 105 ($\mathrm{PhCO^+}$, 100), 94 (6), 84 (8), 77 (23), 65 (5), 49 (12); MS (CI, $\mathrm{NH_3}$) *m/z*: 284 $(\mathrm{M + H})^+$.

*N-[2-(Formyloxy)ethyl]benzamide (7*a*)*

White solid, mp 59-60°C (slightly impure sample, previously reported to be a liquid (30)); IR ($\mathrm{CCl_4}$) $\mathrm{cm^{-1}}$: 3465br (NH), 1735s (OC═O), 1677s (NC═O), 1517m, 1486w, 1302m, 1174s, 909w; ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ: 3.77 (q, ^3J = 5.4 Hz, 2H, $\mathrm{NCH_2}$), 4.39 (t, ^3J = 5.2 Hz, 2H, $\mathrm{OCH_2}$), 6.55 (br s, 1H, NH), 7.35–7.60 (m, 3H, Ar-*m,p*), 7.72–7.84 (m, 2H, Ar-*o*), 8.11 (s, 1H, C(O)H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ: 38.94 ($\mathrm{NCH_2}$), 62.58 ($\mathrm{OCH_2}$), 126.88 (Ar C2, C6), 128.41 (Ar C3, C5), 131.50 (Ar C4), 133.98 (Ar C1), 160.89 (OC═O), 167.79 (NC═O); MS (EI) *m/z*: 193 ($\mathrm{M^+}$, 5), 164 (3), 147 (19), 134 (5), 105 ($\mathrm{PhCO^+}$, 100), 77 (58), 51 (22), 31 (8); MS (CI, $\mathrm{NH_3}$) *m/z*: 211 $(\mathrm{M + NH_3})^+$, 194 $(\mathrm{M + H})^+$.

*N-[3-(Formyloxy)propyl]-benzamide (7*b*) (30)*

The major band collected in an attempt to purify a sample of **3***m* by radial chromatography (20–60% ethyl acetate in hexane) was found to consist, initially, of a mixture of **7***b* and an isomer tentatively identified as **4***b*. The latter was completely converted to **7***b* when the mixture was left in $\mathrm{CDCl_3}$ over 1 month, at or below room temperature. **7***b*: colourless oil; IR ($\mathrm{CCl_4}$) $\mathrm{cm^{-1}}$: 3454m (NH), 1728s (OC═O), 1674s (NC═O), 1605w, 1580w, 1519s, 1487m, 1304w, 1278m, 1176s, 913w, 711m; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ: 1.90–2.08 (m, 2H, $\mathrm{CCH_2C}$), 3.53 (app q, ^3J = 6.4 Hz, 2H, $\mathrm{NCH_2}$), 4.30 (t, ^3J = 6.1 Hz, 2H, $\mathrm{OCH_2}$), 6.66 (br s, 1H, NH), 7.30–7.65 (m, 3H, Ar-*m,p*), 7.70–7.85 (m, 2H, Ar-*o*), 8.10 (s, 1H, C(O)H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ: 28.61 ($\mathrm{CCH_2C}$), 36.58 ($\mathrm{NCH_2}$), 61.48 ($\mathrm{OCH_2}$), 126.82 (Ar C2, C6), 128.55 (Ar C3, C5), 131.47 (Ar C4), 134.36 (Ar C1), 161.21 (HC═O), 167.61 (PhC═O); MS (EI) *m/z*: 207 ($\mathrm{M^+}$, 3), 162 (14), 134 (8), 105 ($\mathrm{PhCO^+}$, 100), 77 (53), 51 (18); MS (CI, $\mathrm{NH_3}$) *m/z*: 225 $(\mathrm{M + NH_4})^+$, 208 $(\mathrm{M + H})^+$.

*N-[3-(Hydroxy)propyl]-N-formylbenzamide (4*b*)*

Obtained as a mixture with **7***b*. ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ: 1.85–ca. 2.0 (m, 2H, $\mathrm{CCH_2C}$), 3.64 (t, ^3J = 5.7 Hz, 2H, $\mathrm{NCH_2}$), 4.04 (t, ^3J = 6.4 Hz, 2H, $\mathrm{OCH_2}$), ca. 7.30–7.85 (Ar), 8.96 (s, 1H, C(O)H); ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$, partial spectrum) δ: 30.70 ($\mathrm{CCH_2C}$), 37.36 ($\mathrm{NCH_2}$), 59.22 ($\mathrm{OCH_2}$), 128.85 (Ar), 129.00 (Ar), 132.35 (Ar), 164.75 (HC═O), 172.90 (PhC═O).

*N-Formyl-N-(2-hydroxyethyl)benzenesulfonamide (4*c*)*

Oxadiazoline **2***g* (143 mg, 0.48 mmol) was heated at 90°C for 48 h in the presence of phenol (69 mg, 0.74 mmol) in 10 mL of benzene. The usual base wash was performed. Compound **4***c* was isolated from the thermolysate by radial chromatography (10–30% ethyl acetate in hexane). IR ($\mathrm{CCl_4}$) $\mathrm{cm^{-1}}$: 3425–3000 (OH), 1736s (C═O), 1449w, 1417w, 1345m ($\mathrm{NSO_2}$), 1264m, 1165s ($\mathrm{NSO_2}$), 1097m, 1027w, 950w, 909w, 858w; ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$, slow exchange) δ: 3.20–3.36 (m, 2H, $\mathrm{NCH_2}$), 4.04–4.26 (m, 2H, $\mathrm{OCH_2}$), 5.03 (br s, 1H, OH), 7.44–7.93 (m, ca. 6H, Ar and C(O)H); ^{13}C NMR (50 MHz, $\mathrm{CDCl_3}$, only peaks from major conformer are given) δ: 41.99 ($\mathrm{NCH_2}$), 62.41 ($\mathrm{OCH_2}$), 126.99 (Ar C2, C6), 129.24 (Ar C3, C5), 132.91 (Ar C4), 139.83 (Ar C1), 160.42 (C═O); MS (EI) *m/z*: 183 (16), 170 (43), 141 ($\mathrm{PhSO_2^+}$, 57), 119 (6), 92 (4), 77 (100), 51 (22), 31 (5); MS (CI, $\mathrm{NH_3}$) *m/z*: 247 $(\mathrm{M + NH_4})^+$, 230 $(\mathrm{M + H})^+$.

Reactions with isocyanates

*Hydantoin 8*a

Oxadiazoline **2***a* (102 mg, 0.60 mmol) was thermolysed in the presence of MeNCO (85 mg, 1.5 mmol) in 10 mL of benzene. Purification by radial chromatography, with 30–40% ethyl acetate in hexane, gave **8***a* in 44% yield. White solid, mp 71–73°C; IR ($\mathrm{CCl_4}$) $\mathrm{cm^{-1}}$: 1785m (C═O), 1729s (C═O), 1461s, 1419m, 1392m, 1299m, 1267w, 1231w, 1184w, 1144w, 1079s, 1015w, 993w, 973w, 949w; ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$) δ: 1.97 (s, 3H, oxazolidine $\mathrm{NCH_3}$), 2.65 (s, 3H, $\mathrm{CH_3}$), 2.73 (s, 3H, $\mathrm{CH_3}$), ca. 2.52–2.77 (overlapped m, 1H, $\mathrm{NCH_2}$), 3.10–3.27 (m, 1H, $\mathrm{NCH_2}$), 3.57–3.72 (m, 1H, $\mathrm{OCH_2}$), 3.77–3.90 (m, 1H, $\mathrm{OCH_2}$); ^{13}C NMR (75 MHz, $\mathrm{C_6D_6}$) δ: 23.06 ($\mathrm{CH_3}$), 23.43 ($\mathrm{CH_3}$), 32.69 ($\mathrm{CH_3}$), 51.18 ($\mathrm{NCH_2}$), 65.17 ($\mathrm{OCH_2}$), 101.67 (spiro C), 155.33 (NC(O)N), 170.24 (N*C*(O)C); MS (EI) *m/z*: 199 ($\mathrm{M^+}$, 1), 171 (M − CO, 4), 154 (16), 141 (4), 127 (9), 113 (92), 99 (2), 86 (21), 70 (36), 57 (100), 42 (71), 28 (36); MS (CI, $\mathrm{NH_3}$) *m/z*: 200 $(\mathrm{M + H})^+$. Anal. calcd. for $\mathrm{C_8H_{13}N_3O}$: C 48.23, H 6.58, N 21.09; found: C 48.03, H 6.81, N 21.00.

*Hydantoin 8*b

Oxadiazoline **2***a* (101 mg, 0.59 mmol) was heated with PhNCO (168 mg, 1.4 mmol) in 10 mL of benzene to give a product that precipitated from the crude thermolysate by addition of 30% ethyl acetate in hexane. After various unsuccessful attempts at recrystallizing the precipitate, it was triturated with the same solvent mixture (27% yield). White solid, mp 156–158°C; IR (KBr) $\mathrm{cm^{-1}}$: 1786w (C═O), 1730s (C═O), 1647w, 1596w, 1494m, 1405m, 1372w, 1278w, 1188w, 1163w, 1069w, 941w, 760w; ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$) δ: 2.20 (s, 3H, $\mathrm{CH_3}$), 2.47–2.58 (m, 1H, $\mathrm{NCH_2}$), 3.10–3.28 (m, 1H, $\mathrm{NCH_2}$), 3.50–3.68 (m, 1H, $\mathrm{OCH_2}$), 3.71–3.86 (m, 1H, $\mathrm{OCH_2}$), 6.93–ca. 7.35 (m, 6H, Ar-*m,p*, overlapped with solvent), 7.46–7.58 (m, 2H, Ar-*o*), 7.58–7.70 (m, 2H, Ar-*o*); ^{13}C NMR (50 MHz, acetone-d_6) δ: 33.28 ($\mathrm{CH_3}$), 52.02 ($\mathrm{NCH_2}$), 66.09 ($\mathrm{OCH_2}$), 103.42 (spiro C), 119.37, 122.80, 127.54, 129.55, 129.67, 132.53, 135.11, 153.72 (NC(O)N), 172.14 (N*C*(O)C) (two Ar peaks are coincident); MS (EI) *m/z*: 323 ($\mathrm{M^+}$, 3), 292 (1), 212 (3), 203 (6), 176 (30), 162 (7), 127 (100), 119 ($\mathrm{PhNCO^+}$, 18), 105 (6), 93 (22), 85 (18), 77 (11), 57 (16); MS (CI, $\mathrm{NH_3}$) *m/z*: 324 $(\mathrm{M + H})^+$; HRMS calcd. for $\mathrm{C_{18}H_{17}N_3O_3}$ ($\mathrm{M^+}$): *m/z* 323.1270; found: *m/z* 323.1262.

*Hydantoin 8*c

Oxadiazoline **2***c* (101 mg, 0.51 mmol) was heated with PhNCO (137 mg, 1.2 mmol) in 10 mL of benzene. The product could not be purified by chromatography due to its low solubility in most common solvents. The crude oil crystallized from a solvent consisting of 20% ethyl acetate in hexane to give **8***c*, as a slightly impure solid, in 87% yield; mp (selected crystals) 132–133°C; IR (KBr) $\mathrm{cm^{-1}}$: 1735s (C═O), 1664m, 1598m, 1557m, 1500m, 1440m, 1411m, 1322m, 1266w, 1201w, 1169w, 1138w, 1111m, 1018w, 980w, 845w, 755m;

^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ: 3.62 (s, 3H, $\mathrm{CH_3}$), 3.52–3.70 (m, 1H, $\mathrm{NCH_2}$), 4.03–4.18 (m, 1H, $\mathrm{NCH_2}$), 4.23–4.54 (m, 2H, $\mathrm{OCH_2}$), 7.08–7.55 (m, 10H, Ar); ^{13}C NMR (50 MHz, $\mathrm{C_6D_6}$) δ: 24.00 ($\mathrm{CH_3}$), 43.76 ($\mathrm{NCH_2}$), 68.69 ($\mathrm{OCH_2}$), 109.88 (spiro C), 119–139 (Ar, overlapped with solvent), 157.14 (NC(O)N), 164.80 (N*C*(O)C), 167.64 (N*C*(O)$\mathrm{CH_3}$); MS (EI) *m*/*z*: 248 (2), 220 (52), 217 (3), 178 (1), 146 (2), 133 (1), 119 ($\mathrm{PhNCO^+}$, 100), 101 (24), 91 (22), 77 (3), 71 (18), 64 (11), 56 (23), 51 (4), 42 (13), 28 (4); MS (CI, $\mathrm{NH_3}$) did not give useful information.

*Hydantoin 8*d

Oxadiazoline **2***d* (115 mg, 0.51 mmol) was heated in the presence of PhNCO (136 mg, 1.1 mmol) in 10 mL of benzene. The product was obtained as a pale yellow solid in 72% yield after washing with ethyl acetate – hexane. Crystals obtained from recrystallization in the same solvent mixture melted at 240–241°C. IR ($\mathrm{CCl_4}$) cm^{-1}: 1805w (hydantoin C═O), 1747s (hydantoin C═O), 1679m (methacryloyl C═O), 1624w, 1598w, 1502w, 1438w, 1400m, 1322m, 1246w, 1167m, 1138w, 1107w, 1080m, 1050m, 911w, 853w; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ: 1.63 (s, 3H, $\mathrm{CH_3}$), 3.48–3.63 (m, 1H, $\mathrm{NCH_2}$), 4.02–4.13 (m, 1H, $\mathrm{NCH_2}$), 4.25–4.38 (m, 1H, $\mathrm{OCH_2}$), 4.43–4.54 (m, 1H, $\mathrm{OCH_2}$), 5.22 (s, 1H, ═$\mathrm{CH_2}$), 5.29 (s, 1H, ═$\mathrm{CH_2}$), 6.64 (d, ^{3}J = 7.5 Hz, 2H, Ar), 6.85–7.60 (m, 8H, Ar); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ: 20.20 ($\mathrm{CH_3}$), 43.82 ($\mathrm{NCH_2}$), 69.75 ($\mathrm{OCH_2}$), 109.00 (spiro C), 119–130 (overlapping signals), 131.05, 134.08, 145.83 (═$\mathrm{CR_2}$), 156.17 (NC(O)N), 157.32 (methacryloyl C═O), 163.57 (N*C*(O)C); MS (EI) *m*/*z*: 377 ($\mathrm{M^+}$, 3), 258 (5), 230 (32), 217 (26), 202 (6), 173 (22), 146 (10), 139 (12), 119 ($\mathrm{PhNCO^+}$, 100), 112 (15), 98 (11), 91 (40), 77 (12), 69 (86), 64 (16), 42 (62); MS (CI, $\mathrm{NH_3}$) *m*/*z*: 378 (M + H)$^+$; HRMS calcd. for $\mathrm{C_{14}H_{14}N_2O_3}$ (M − PhNCO): *m*/*z* 258.1004; found: *m*/*z* 258.1010.

*Hydantoin 8*e

Oxadiazoline **2***e* (90 mg, 0.35 mmol) was heated with PhNCO (132 mg, 1.1 mmol) in 10 mL of benzene. The sparingly soluble oily product crystallized after addition of ethyl acetate, and it was then recrystallized from the same solvent (76% yield). White solid, mp 151–152°C; IR (KBr) cm^{-1}: 1796w (hydantoin C═O), 1741s (hydantoin C═O), 1667m (PhC═O), 1594w, 1501w, 1451w, 1398m, 1326w, 1292w, 1240w, 1168w, 1141w, 1111w, 1079m, 1043m, 911w, 852w, 768w, 748w; ^{1}H NMR (300 MHz, acetone-d_6) δ: 3.72–3.86 (m, 1H, $\mathrm{NCH_2}$), 4.13–4.28 (m, 1H, $\mathrm{NCH_2}$), 4.47–4.60 (m, 1H, $\mathrm{OCH_2}$), 4.60–4.73 (m, 1H, $\mathrm{OCH_2}$), 6.62–6.74 (m, 2H, Ar), 6.95–7.06 (m, 1H, Ar), 7.13–7.50 (m, 12H, Ar); ^{13}C NMR (75 MHz, acetone-d_6) δ: 44.73 ($\mathrm{NCH_2}$), 70.88 ($\mathrm{OCH_2}$), 110.53 (spiro C), 121.80, 124.45, 127.43, 128.79, 129.13, 129.18, 129.63, 129.94, 130.23, 131.85, 132.74, 147.28, 156.31 (NC(O)N), 157.79 (PhC(O)N), 164.41 (N*C*(O)C); MS (EI) *m*/*z*: 216 (34), 189 (8), 146 (8), 119 ($\mathrm{PhNCO^+}$, 100), 105 ($\mathrm{PhCO^+}$, 57), 98 (13), 91 (28), 86 (37), 84 (56), 77 (38), 70 (37). Anal. calcd. for $\mathrm{C_{24}H_{19}N_3O_4}$: C 69.72, H 4.63; found: C 69.33, H 4.86.

*Hydantoin 8*f

Oxadiazoline **2***h* (100 mg, 0.36 mmol) was heated with MeNCO (54 mg, 0.95 mmol) in 10 mL of benzene. The product, crystallized from the crude oil upon addition of ethyl acetate – hexane, was washed with 10% ethyl acetate in hexane (78% yield). White solid, mp 87–89°C; IR ($\mathrm{CCl_4}$) cm^{-1}: 1794w (hydantoin C═O), 1734s (hydantoin C═O), 1673m (PhC═O), 1465m, 1396w, 1334w, 1298w, 1273w, 1231w, 1169w, 1140w, 1081w, 1056m, 962w, 924w; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ: 1.57–1.72 (m, 1H, $\mathrm{CCH_2C}$), 1.90–2.13 (m, 1H, $\mathrm{CCH_2C}$), 3.12 (s, 3H, $\mathrm{CH_3}$), 3.25 (s, 3H, $\mathrm{CH_3}$), ca. 2.98–3.32 (overlapped m, 1H, $\mathrm{NCH_2}$), 4.02–4.22 (m, 3H, $\mathrm{NCH_2}$, $\mathrm{OCH_2}$), 7.37–7.62 (m, 5H, Ar); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ: 23.89 ($\mathrm{CH_3}$), 24.74 ($\mathrm{CH_3}$), 35.22 and 35.36 (C*C*$\mathrm{H_2}$C and $\mathrm{NCH_2}$), 63.62 ($\mathrm{OCH_2}$), 126.80, 128.16, 128.52, 131.48, 135.23, 154.90 (NC(O)N), 169.05 (PhC(O)N), 174.48 (N*C*(O)C) (some aromatic Cs overlap); MS (EI) *m*/*z*: 303 ($\mathrm{M^+}$, 1), 198 (2), 190 (4), 169 (100), 141 (9), 118 (6), 113 (5), 105 ($\mathrm{PhCO^+}$, 13), 84 (14), 77 (15), 56 (15); MS (CI, $\mathrm{NH_3}$) *m*/*z*: 304 (M + H)$^+$. Anal. calcd. for $\mathrm{C_{15}H_{17}N_3O_4}$: C 59.40, H 5.65; found: C 59.20, H 6.00.

Reactions with alkynes

*Thermolysis of 2*e *with DMAD*

Oxadiazoline **2***e* (187 mg, 0.72 mmol) was heated with DMAD (217 mg, 1.5 mmol) in 14 mL of benzene. The products were separated by chromatography, with ethyl acetate – hexane as elution solvent.

*Oxazoline 9*a: White solid isolated in 73% yield, mp 109–111°C. IR ($\mathrm{CCl_4}$) cm^{-1}: 1745s (OC═O's), 1688s (PhC═O), 1645m (C═N), 1611m (C═C), 1507w, 1443m, 1381w, 1242s, 1115m, 1028s, 976w, 910m, 879w, 843w; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ: 3.73 (s, 3H, $\mathrm{OCH_3}$), 3.96 (s, 3H, $\mathrm{OCH_3}$), 3.86 (app dt, *J* ~ 1 Hz, ^{3}J = 6.5 Hz, 2H, $\mathrm{NCH_2}$), 4.04 (app dt, *J* ~ 1Hz, ^{3}J = 6.5 Hz, 2H, $\mathrm{OCH_2}$), 7.44–7.56 (m, 2H, Ar-*m*), 7.57–7.65 (m, 1H, Ar-*p*), 7.86–7.94 (m, 2H, Ar-*o*); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ: 53.26 (2 × $\mathrm{OCH_3}$, coincident signals), 55.13 ($\mathrm{NCH_2}$), 68.42 ($\mathrm{OCH_2}$), 128.71 and 128.76 (Ar C2, C6 and Ar C3, C5), 132.60 (Ar C4), 133.76 and 135.73 and 137.02 (Ar C1 and C═C), 159.87 and 163.02 and 164.55 (2 × OC═O and oxazoline C2), 190.02 (PhC═O); MS (EI) *m*/*z*: 317 ($\mathrm{M^+}$, 20), 302 (M − $\mathrm{CH_3}$, 10), 288 (63), 257 (16), 230 (38), 199 (17), 171 (24), 105 ($\mathrm{PhCO^+}$, 100), 77 (87); MS (CI, $\mathrm{NH_3}$) *m*/*z*: 318 (M + H)$^+$; HRMS calcd. for $\mathrm{C_{16}H_{15}NO_6}$ ($\mathrm{M^+}$): *m*/*z* 317.0899; found: *m*/*z* 317.0901.

*Dihydrofuran 11*a: Isolated in 4% yield. IR ($\mathrm{CCl_4}$) cm^{-1}: 2257w (C≡C), 1741s (OC═O's), 1637m (NC═O), 1577w, 1494w, 1437m, 1361m, 1254s, 1210m, 1119m, 1067w, 1020m, 995m, 909m; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ: 3.35–3.45 (m, 1H, $\mathrm{NCH_2}$), ca. 3.60–3.75 (overlapped m, 1H, $\mathrm{NCH_2}$), 3.62 (s, 3H, $\mathrm{OCH_3}$), 3.77 (s, 3H, $\mathrm{OCH_3}$), 3.83 (s, 3H, $\mathrm{OCH_3}$), 3.85 (s, 3H, $\mathrm{OCH_3}$), 4.22–4.42 (m, 2H, $\mathrm{OCH_2}$), 7.35–7.50 (m, 3H, Ar-*m*,*p*), 7.76–7.84 (m, 2H, Ar-*o*); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ: 48.34 ($\mathrm{NCH_2}$), 51.21 ($\mathrm{OCH_3}$), 52.21 ($\mathrm{OCH_3}$), 52.83 ($\mathrm{OCH_3}$), 53.11 ($\mathrm{OCH_3}$), 69.42 (≡C), 69.64 ($\mathrm{OCH_2}$), 104.09 (≡C), 120.76 (*C*(C)(C)(O)(O)), 127–131 (overlapping peaks, Ar and ═C), 142.86 (═C), 161.02 and 163.69 and 163.80 and 165.32 and 166.81 (3 × OC═O, PhC═O, and spiro C); MS (EI) *m*/*z*: 400 (M − $\mathrm{CO_2Me}$, 16), 354 (M − C(O)Ph, 100), 344 (8), 105 ($\mathrm{PhCO^+}$, 54), 77 (20); MS (CI, $\mathrm{NH_3}$) *m*/*z*: 460 (M + H)$^+$.

*Unidentified 1:2 adduct (1*e*:DMAD)*: Isolated in 4% yield. IR ($\mathrm{CCl_4}$) cm^{-1}: 1776m (C═O), 1737s (C═O), 1697m (C═O), 1582w, 1506m, 1441m, 1338w, 1232s, 1122m, 1012w, 949w, 910w; ^{1}H NMR (300 MHz, CDCl$_3$) δ: 3.53 (s, 3H, OCH$_3$), 3.72 (s, 3H, OCH$_3$), 3.74 (s, 3H, OCH$_3$), 3.82 (s, 3H, OCH$_3$), 4.49 (t, ^3J = 8.1 Hz, 2H, NCH$_2$), 4.98 (t, ^3J = 8.1 Hz, 2H, OCH$_2$), 7.32–7.47 (m, 5H, Ar); ^{13}C NMR (75 MHz, CDCl$_3$) δ: 45.90 (OCH$_3$), 51.67 (OCH$_3$), 51.86 (OCH$_3$), 55.28 (OCH$_3$), 75.06 (NCH$_2$), 92.26 (OCH$_2$), 111.43, 114.58, 124.23, 127.98, 128.07, 129.00, 129.53, 131.18, 134.81, 151.61, (152.48), 152.65, 160.20, 164.12, 167.23; MS (EI) *m/z*: 459 (M$^+$, 35), 428 (M − OCH$_3$, 6), 415 (6), 400 (M − CO$_2$CH$_3$, 12), 384 (23), 372 (20), 369 (6), 356 (4), 344 (30), 340 (3), 326 (6), 310 (5), 298 (6), 282 (7), 268 (6), 252 (11), 236 (6), 151 (12), 105 (PhCO$^+$, 100), 84 (39), 77 (56), 61 (18), 49 (39); MS (CI, NH$_3$) did not give useful information; HRMS calcd. for C$_{22}$H$_{21}$NO$_{10}$ (M$^+$): *m/z* 459.1165; found: *m/z* 459.1159.

Alcoholysis of **9**a

Compound **9**a (1.12 g, 3.5 mmol) was stirred in 10 mL of 0.1 M acetic acid in methanol for 13 days at room temperature. After evaporation of the solvent, the oil was redissolved in 20 mL of CH$_2$Cl$_2$, and washed successively with NaHCO$_3$ (5%, 4 × 10 mL) and water, and the combined organic layers were dried over MgSO$_4$. Separation by radial chromatography, using 10–50% ethyl acetate in hexane, gave a mixture of two inseparable products, **12** and an isomer tentatively identified as **13**, in a ratio of ca. 70:30. The spectral data shown below are those of the mixture.

*(Z)-3-Oxo-3-phenyl-1-propene-1,1,2-tricarboxylic acid, trimethyl ester (**12**)* Lit. (27): mp 66–68°C; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 3.65 (s, 3H, OCH$_3$), 3.75 (s, 3H, OCH$_3$), 3.94 (s, 3H, OCH$_3$), ca. 7.35–7.70 (m, 3H, Ar-*m,p*), ca. 7.84–7.98 (m, 2H, Ar-*o*); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 52.4–53.6 (overlapped OCH$_3$'s), 128.67 and 128.91 (Ar C2, C6 and Ar C3, C5), 134.09 (Ar C4), 135.19 (Ar C1), 142.44 (=C; other alkene C not observed due to low S/N), 161.94 (OC=O), 162.63 (OC=O), 163.94 (OC=O), 190.00 (PhC=O); MS (EI) *m/z*: 306 (M$^+$, 16), 275 (M − OCH$_3$, 12), 247 (M − CO$_2$CH$_3$, 3), 229 (1), 215 (1), 198 (1), 157 (1), 129 (3), 105 (PhCO$^+$, 100), 77 (41), 59 (5), 51 (8), 44 (3), 29 (1).

*4,5-Dihydro-4-methoxy-5-oxo-2-phenyl-3,4-furandicarboxylic acid, dimethyl ester (**13**a)*: ^{1}H NMR (200 MHz, CDCl$_3$) δ: 3.50 (s, 3H, OCH$_3$), 3.79 (s, 3H, OCH$_3$), 3.92 (s, 3H, OCH$_3$), ca. 7.35–7.70 (m, 5H, Ar); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 52.4–53.6 (overlapped OCH$_3$'s), 107.50, 126.22, 126.93, 129.28, 130.21, 133.16, 135.06, (157.05), 159.71 (OC=O), 160.44 (OC=O), 164.17 (OC=O); MS (EI) *m/z*: 306 (M$^+$, 8), 275 (M − OCH$_3$, 39), 247 (M − CO$_2$CH$_3$, 38), 230 (91), 215 (70), 203 (34), 187 (15), 175 (8), 157 (13), 151 (5), 144 (10), 140 (10), 129 (15), 111 (19), 105 (PhCO$^+$, 100), 102 (11), 91 (5), 82 (5), 77 (62), 59 (19), 51 (15), 39 (12), 29 (4).

Thermolysis of **2**e *with methyl propiolate*

Oxadiazoline **2**e (187 mg, 0.72 mmol) was heated with methyl propiolate (67 mg, 0.80 mmol) in 14 mL of benzene. By ^{1}H NMR, the product mixture was found to consist mainly of **14**. Substantial decomposition of the product occurred during the two successive separations (radial chromatography, ethyl acetate – hexane). Consequently, **14** was obtained in only 4% yield.

*Oxazoline **14***: ^{1}H NMR (200 MHz, CDCl$_3$) δ: 3.76 (s, 3H, OCH$_3$), 3.87 (app t, ^3J = 8.9 Hz, 2H, NCH$_2$), 4.06 (app t, ^3J = 8.9 Hz, 2H, OCH$_2$), 7.37 (s, 1H, =C-H), ca. 7.35–7.65 (overlapped m, 3H, Ar-*m,p*), 7.81–7.95 (m, 2H, Ar-*o*); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 53.05 (OCH$_3$), 55.17 (NCH$_2$), 68.21 (OCH$_2$), 127.66 (=C-H), 128.66 and 128.89 (Ar C2, C6 and Ar C3, C5), 133.63 (Ar C4), 136.07 and 139.90 (Ar C1 and =CR$_2$), 162.20 (oxazoline C2), 164.18 (OC=O), 192.27 (PhC=O); MS (EI) *m/z*: 259 (M$^+$, 22), 230 (100), 216 (45), 172 (27), 128 (9), 105 (PhCO$^+$, 63), 84 (24), 77 (55), 49 (16); MS (CI, NH$_3$) *m/z*: 260 (M + H)$^+$; HRMS calcd. for C$_{14}$H$_{13}$NO$_4$ (M$^+$): *m/z* 259.0845; found: *m/z* 259.0857.

Thermolysis of **2**d *with DMAD*

Thermolysis of oxadiazoline **2**d (112 mg, 0.50 mmol) in the presence of DMAD (146 mg, 1.0 mmol) in 10 mL of benzene gave a thermolysate that was found (by ^{1}H NMR) to consist almost entirely of **9**b, in addition to the excess DMAD. Repeated separations by radial chromatography (ethyl acetate – hexane) gave pure **9**b in 54% yield.

*Oxazoline **9**b*: IR (CCl$_4$) cm^{-1}: 1745s (OC=O's), 1682s (NC=O's), 1644m, 1611m, 1435m, 1379m, 1321m, 1285m, 1251s, 1152m, 1055m, 1026m, 976w, 909m, 877w, 845w; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 1.95 (s, 3H, CCH$_3$), 3.76 (s, 3H, OCH$_3$), 3.90 (s, 3H, OCH$_3$), 3.95 (app dt, $J \sim 1$ Hz, ^3J = 9.4 Hz, NCH$_2$), 4.25 (app dt, $J \sim 1$ Hz, ^3J = 9.4 Hz, OCH$_2$), 5.82 (app d, ^4J = 0.7 Hz, 1H, =CH$_2$), 5.92 (app d, ^4J = 1.4 Hz, 1H, =CH$_2$); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 16.66 (C*C*H$_3$), 53.23 (2 × OCH$_3$, coincident signals), 55.22 (NCH$_2$), 68.50 (OCH$_2$), 128.30 (=CH$_2$), 132.20 and 137.44 (tetrasubstituted alkene C's), 144.36 (H$_2$C=*C*R$_2$), 160.00 (oxazoline C2), 163.09 (OC=O), 164.57 (OC=O), 191.69 (ketone C=O); MS (EI) *m/z*: 282 (M + H$^+$, 8), 266 (M − CH$_3$, 8), 252 (100), 241 (19), 239 (18), 222 (30), 208 (23), 194 (30), 190 (18), 181 (6), 163 (25), 154 (7), 135 (31), 124 (9), 111 (22), 96 (8), 84 (36), 71 (34), 59 (26), 49 (28), 45 (37), 41 (70); MS (CI, NH$_3$) *m/z*: 282 (M + H)$^+$; HRMS calcd. for C$_{13}$H$_{16}$NO$_6$ (M + H$^+$): *m/z* 282.0978; found: 282.0966.

Thermolysis of **2**c *with DMAD*

Oxadiazoline **2**c (99 mg, 0.50 mmol) was heated with DMAD (158 mg, 1.1 mmol) in 12 mL of benzene. ^{1}H NMR analysis of the crude thermolysate revealed **9**c to be the major product. Repeated separations by radial chromatography, with mixtures of ethyl acetate and hexane as elution solvent, gave the five 1:2 (carbene:DMAD) adducts described below. The major product could not be recovered, presumably due to its decomposition on the silica plate.

*Oxazoline **9**c*: Not isolated, data from crude thermolysate; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 2.45 (s, 3H, C(O)CH$_3$), 3.82 (s, 3H, OCH$_3$), 3.91 (s, 3H, OCH$_3$), 4.03 (app dt, $J \sim 1$ Hz, ^3J = 9.4 Hz, 2H, NCH$_2$), 4.37 (app dt, $J \sim 1$ Hz, ^3J = 9.4 Hz, 2H, OCH$_2$); MS (EI) *m/z*: 255 (M$^+$, 7), 240 (M − CH$_3$, 100), 224 (M − OCH$_3$, 27), 208 (55), 196 (19), 182 (20), 168 (20), 154 (32), 140 (8), 125 (37), 111 (62), 97 (34), 80 (17), 66 (26), 59 (28), 53 (18), 43 (64), 39 (20), 29 (11).

*Dihydrofuran **11**b*: Pale yellow oil, isolated in 22% yield. IR (CCl$_4$) cm^{-1}: 1740s (C=O's), 1643m, 1559m, 1437m, 1386w, 1322m, 1288s, 1254s, 1223s, 1164m, 1126w, 1082m, 1045m; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 1.83 (s, 3H, C(O)CH$_3$), 3.68 (s, 3H, OCH$_3$), 3.77 (s, 3H, OCH$_3$), 3.80 (s, 3H, OCH$_3$), 3.86 (s, 3H, OCH$_3$), ca. 3.60–3.90 (overlapped m, 2H, NCH$_2$), 4.27–4.57 (m, 2H, OCH$_2$); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 19.07 (C(O)*C*H$_3$), 45.34 (NCH$_2$), 51.60 (OCH$_3$), 52.32 (OCH$_3$), 52.57 (OCH$_3$), 53.01 (OCH$_3$), 67.65 (OCH$_2$), 81.97 (alkyne), 104.08 (alkyne), 114.03 (*C*(C)(C)(O)(O)), 125.22 (alkene), 140.89 and 144.04 (alkene and spiro C), 161.49 (C═O), 162.43 (C═O), 163.73 (C═O), 164.47 (C═O); MS (EI) *m/z*: 366 (M − OCH$_3$, 6), 354 (M − C(O)CH$_3$, 100), 338 (M − CO$_2$CH$_3$, 7), 237 (6), 179 (10), 84 (35), 59 (12), 49 (21); MS (CI, NH$_3$) *m/z*: 415 (M + NH$_4$)$^+$, 398 (M + H)$^+$.

*Dihydrofuran **11**c*: Isolated as a partially solidified oil in 29% yield. IR (CCl$_4$) cm^{-1}: 1740s (C═O's), 1655m, 1624w, 1438m, 1382w, 1358w, 1332w, 1253s, 1204m, 1139m, 1111w, 1053w, 995m, 934w, 906w, 882w; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 2.28 (s, 3H, C(O)CH$_3$), 3.23–3.38 (m, 1H, NCH$_2$), ca. 3.56–3.70 (overlapped m, 1H, NCH$_2$), 3.64 (s, 3H, OCH$_3$), 3.73 (s, 3H, OCH$_3$), 3.78 (s, 3H, OCH$_3$), 3.81 (s, 3H, OCH$_3$), 4.14–4.37 (m, 2H, OCH$_2$); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 14.18 (C(O)*C*H$_3$), 48.37 (NCH$_2$), 51.03 (OCH$_3$), 52.15 (OCH$_3$), 52.75 (OCH$_3$), 53.01 (OCH$_3$), 68.10 (alkyne), 69.52 (OCH$_2$), 104.48 (alkyne), 121.35 (*C*(C)(C)(O)(O)), 130.60 (alkene C), 142.26 (alkene C), 160.90 and 163.76 and 164.13 and 166.67 and 168.77 (4 × C═O, spiro C); MS (EI) *m/z*: 397 (M$^+$, 2), 366 (M − OCH$_3$, 4), 354 (M − C(O)CH$_3$, 100), 338 (M − CO$_2$CH$_3$, 7), 322 (3), 310 (6), 278 (3), 264 (3), 250 (14), 236 (3), 218 (14), 204 (2), 192 (3), 176 (3), 165 (2), 150 (2), 135 (3), 118 (2), 106 (2), 91 (2), 77 (2), 59 (12), 43 (9); MS (CI, NH$_3$) *m/z*: 398 (M + H)$^+$; HRMS calcd. for C$_{16}$H$_{16}$NO$_9$ (M − OCH$_3$): *m/z* 366.0825; found: *m/z* 366.0816.

*Unidentified 1:2 adduct (**1**c:DMAD)*: Isolated as a solid in 4% yield. IR (CCl$_4$) cm^{-1}: 1743s (C═O's), 1601w, 1521w, 1436m, 1397w, 1332m, 1293m, 1244m, 1209s, 1133m, 1072w, 910w; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 2.31 (s, 3H, C(O)CH$_3$), ca. 3.6–4.0 (overlapped m, 1H?, NCH$_2$),[16] 4.05–4.25 (m, 1H, NCH$_2$), 4.50–4.65 (m, 2H, OCH$_2$), 3.72 (s, 3H, OCH$_3$), 3.76 (s, 3H, OCH$_3$), 3.79 (s, 3H, OCH$_3$), 3.95 (s, 3H, OCH$_3$); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 17.51 (C(O)*C*H$_3$), 44.11 (NCH$_2$), 51.77 (OCH$_3$), 52.09 (OCH$_3$), 53.57 (OCH$_3$), 54.10 (OCH$_3$), 67.23 (OCH$_2$), 68.04, 107.67, 111.61, 139.51, 145.05, 163.30, 163.73, 165.35, 166.19, 168.62; MS (EI) *m/z*: 397 (M$^+$, 1), 366 (M − OCH$_3$, 10), 353 (1), 338 (M − CO$_2$CH$_3$, 100), 306 (5), 235 (6), 221 (6), 163 (10), 84 (9), 61 (4), 49 (7); MS (CI, NH$_3$) *m/z*: 415 (M + NH$_4$)$^+$, 398 (M + H)$^+$; HRMS calcd. for C$_{16}$H$_{16}$NO$_9$ (M − OCH$_3$): *m/z* 366.0825, found: *m/z* 366.0809.

*Unidentified 1:2 adduct (**1**c:DMAD)*: Isolated as a solid in ca. 1% yield. IR (CCl$_4$) cm^{-1}: 1769s (C═O), 1730s (C═O), 1695s (NC═O), 1651w, 1592w, 1505m, 1445m, 1378w, 1335m, 1246s, 1211m, 1158m, 1123m, 1065w, 1007w; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 2.49 (s, 3H, C(O)CH$_3$), 3.69 (s, 3H, OCH$_3$), 3.77 (s, 3H, OCH$_3$), 3.81 (s, 3H, OCH$_3$), 3.82 (s, 3H, OCH$_3$), 4.47 (app t, ^3J = 8.0 Hz, 2H, NCH$_2$), 4.95 (app t, ^3J = 8.0 Hz, 2H, OCH$_2$); MS (EI) *m/z*: 354 (M − C(O)CH$_3$, 18), 84 (100); MS (CI, NH$_3$) *m/z*: 415 (M + NH$_4$)$^+$, 398 (M + H)$^+$.

*Unidentified 1:2 adduct (**1**c:DMAD)*: Isolated as an oil in 6% yield. IR (CCl$_4$) cm^{-1}: 1748s (C═O), 1719s (C═O), 1597m, 1477w, 1437m, 1421m, 1353w, 1298m, 1236s, 1196m, 1144m, 1057w; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 2.42 (s, 3H, C(O)CH$_3$), 3.71 (s, 3H, OCH$_3$), 3.73 (s, 3H, OCH$_3$), 3.76 (s, 3H, OCH$_3$), 3.90 (s, 3H, OCH$_3$), ca. 3.55–3.90 (overlapped m, ~2H, NCH$_2$). 4.62 (app t, ^3J = 7.8 Hz, 2H, OCH$_2$); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 27.71 (C(O)*C*H$_3$), 44.82 (NCH$_2$), 51.49 (OCH$_3$), 52.30 (OCH$_3$), 52.81 (OCH$_3$), 53.39 (OCH$_3$), 62.39, 68.34 (OCH$_2$), 80.97, 102.44, 107.49, 110.04, 137.52, 156.35, 163.21, 165.44, 166.22, 171.60, 203.94; MS (EI) *m/z*: 366 (M − OCH$_3$, 6), 354 (M − C(O)CH$_3$, 100), 338 (M − CO$_2$CH$_3$, 6), 237 (6), 179 (8), 121 (6), 84 (6), 59 (5), 49 (4); MS (CI, NH$_3$) *m/z*: 415 (M + NH$_4$)$^+$, 398 (M + H)$^+$.

*Thermolysis of **2**g with DMAD*

Oxadiazoline **2g** (297 mg, 1.00 mmol) was heated with DMAD (310 mg, 2.18 mmol) in 16 mL of benzene. The products were separated by radial chromatography (ethyl acetate – hexane).

*3-(Phenylsulfonyl)-2-oxazolidinone (**15**) (ref. 31)*: Isolated in 23% yield, mp 136–138°C; IR (CCl$_4$) cm^{-1}: 1801s, 1480w, 1450w, 1382m (NSO$_2$), 1264w, 1180s (NSO$_2$), 1147s, 1094w, 1050w, 909w; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 4.00–4.15 (m, 2H, NCH$_2$), 4.32–4.46 (m, 2H, OCH$_2$), 7.50–7.80 (m, 3H, Ar-*m,p*), 8.02–8.13 (m, 2H, Ar-*o*); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 44.61 (NCH$_2$), 62.28 (OCH$_2$), 128.26 (Ar C2, C6), 129.30 (Ar C3, C5), 134.55 (Ar C4), 136.81 (Ar C1), 151.91 (C═O); MS (EI) *m/z*: 163 (30), 141 (PhSO$_2^+$, 12), 118 (8), 104 (53), 91 (6), 77 (100), 56 (6), 51 (28), 28 (2); MS (CI, NH$_3$) *m/z*: 245 (M + NH$_4$)$^+$.

*Dimethyl 3,3-dimethyl-3*H*-pyrazole-4,5-dicarboxylate (**16**) (ref. 26)*: Isolated in 13% yield. IR (CCl$_4$) cm^{-1}: 1732s (C═O), 1647w, 1438w, 1334w, 1264s, 1198w, 1167w, 1114w, 1033w, 909m; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 1.58 (s, 6H, C(CH$_3$)$_2$), 3.92 (s, 3H, OCH$_3$), 4.00 (s, 3H, OCH$_3$); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 20.86 (C(*C*H$_3$)$_2$), 52.98 (2 × OCH$_3$, coincident), 97.46 (C3), 144.68 (C4), 153.56 (C5), 160.81 (C═O), 162.97 (C═O); MS (EI) *m/z*: 183 (3), 169 (3), 152 (33), 141 (50), 125 (36), 109 (34), 93 (55), 79 (65), 67 (100), 59 (43), 53 (31), 39 (50), 29 (18).

*Cyclopentadiene **17***: Obtained as a pale yellow oil in 3% yield. IR (CCl$_4$) cm^{-1}: 1730s (C═O), 1649w, 1437m, 1368m (NSO$_2$), 1342m, 1262s, 1203m, 1169m (NSO$_2$), 1096w, 1015w, 995w, 909s; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 3.58 (s, 6H, OCH$_3$), 3.89 (s, 6H, OCH$_3$), 3.97 (t, ^3J = 6.5 Hz, 2H, NCH$_2$), 4.39 (t, ^3J = 6.5 Hz, 2H, OCH$_2$), 7.42–7.65 (m, 3H, Ar-*m,p*), 7.80–7.88 (m, 2H, Ar-*o*); ^{13}C NMR (50 MHz, CDCl$_3$) δ: 47.66 (NCH$_2$), 52.08 (OCH$_3$), 52.85 (OCH$_3$), 67.44 (OCH$_2$), 101.18 (spiro C), 127.78 (Ar C2, C6), 128.97 (Ar C3, C5), 132.80 (Ar C4), 138.29 (probably Ar C1), 139.00 (probably ═*C*-C-*C*═), 140.32 (probably ═C-C═), 160.45

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[16] The following resonances were also observed, which could account for one of the NCH$_2$ protons: δ 3.56 (app t, *J* = 2.3 Hz, ~0.5H) and 3.62 (app t, *J* = 2.3 Hz, ~0.5H) (slow exchange is expected in these compounds); alternatively, these could be due to impurities.

(C=O), 162.60 (C=O); MS (EI) *m/z*: 495 (M^+, 2), 464 (M − OCH_3, 5), 431 (3), 354 (M − SO_2Ph, 30), 322 (28), 310 (49), 290 (14), 264 (30), 182 (12), 141 ($PhSO_2^+$, 15), 84 (26), 77 (100), 59 (27); MS (CI, NH_3) *m/z*: 513 $(M + NH_4)^+$; HRMS calcd. for $C_{21}H_{21}NO_{11}S$ (M^+): *m/z* 495.0835, found: *m/z* 495.0835.

N-*Formyl*-N-*[2-(formyloxy)ethyl]benzenesulfonamide* ***18***: IR (CCl_4) cm^{-1}: 1737s (C=O), 1710s (C=O), 1449w, 1401w, 1371m (NSO_2), 1311w, 1286w, 1232w, 1172s (NSO_2), 1091w, 1013w, 975w, 944w; ^1H NMR (200 MHz, $CDCl_3$) δ: 3.79 (t, ^3J = 5.7 Hz, 2H, NCH_2), 4.28 (t, ^3J = 5.7 Hz, 2H, OCH_2), 7.50–7.80 (m, 3H, Ar-*m,p*), 7.81–8.00 (m, 3H, Ar-*o* and NC(O)H), 9.15 (s, 1H, OC(O)H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 41.00 (NCH_2), 60.21 (OCH_2), 127.45 (Ar C2, C6), 129.80 (Ar C3, C5), 134.47 (Ar C4), 137.80 (Ar C1), 160.26 (C=O), 161.28 (C=O); MS (EI) *m/z*: 230 (2), 186 (4), 170 (10), 141 ($PhSO_2^+$, 36), 94 (58), 84 (42), 77 (100), 49 (37); MS (CI, NH_3) *m/z*: 275 $(M + NH_4)^+$.

*Unidentified 1:3 adduct (**1**g:DMAD)*: Isolated in ca. 1% yield. IR (CCl_4) cm^{-1}: 1748s (C=O), 1607m, 1500m, 1469w, 1435m, 1362w (NSO_2), 1343w, 1259s, 1164m (NSO_2), 1108w, 1025m; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.31 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), (NCH_2 overlapped with OCH_3's), 4.72–4.84 (m, 2H, OCH_2), 7.52–7.72 (m, 3H, Ar-*m,p*), 7.99–8.05 (m, 2H, Ar-*o*); ^{13}C NMR (50 MHz, $CDCl_3$, partial spectrum) δ: 46.21 (NCH_2), 51.38 (OCH_3), 51.56 (OCH_3), 52.46 (OCH_3), 53.49 (OCH_3), 54.06 (OCH_3), 54.25 (OCH_3), 69.43 (NCH_2), 128.82 and 128.88 (Ar C2, C6 and Ar C3, C5), 134.40 (probably Ar C4), 139.56, 145.33, 161–168 (several overlapping peaks); MS (EI) *m/z*: 606 (M − OCH_3, 5), 578 (M − CO_2CH_3, 100), 438 (5), 394 (6), 378 (11), 364 (6), 354 (18), 320 (7), 141 ($PhSO_2^+$, 8), 77 (35), 59 (18); MS (CI, NH_3) *m/z*: 638 $(M + H)^+$.

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