Thermolysis of a spiro-fused oxadiazoline: The carbonyl ylide–cyclic carbene–diradical sequence

Nadine Merkley and John Warkentin

Abstract: Thermolysis of spiro-fused oxadiazoline **1** in benzene led to loss of N_2 to form a carbonyl ylide intermediate. Most of the ylide fragmented to acetone and 4-phenyl-1,3-dioxane-2-ylidene, which could be trapped with *tert*-butyl alcohol. In the absence of the trapping agent, the major pathway followed by the carbene was fragmentation to a diradical, 5-phenyl-2-oxa-1-oxo-1,5-pentanediyl. The latter diradical coupled to α-phenyl-γ-butyrolactone and decarboxylated to afford cyclopropylbenzene. Other products from the reaction were those of *apparent* insertion of the carbene into a C–H bond of the benzene solvent and into a C–H bond of acetone. Such reactions appear to be without precedent — alternative, non-carbene mechanisms are proposed.

Key words: dioxacarbene, carbonyl ylide, cyclopropylbenzene, diradical, lactone, oxadiazoline.

Résumé : La thermolyse de l'oxadiazoline à fusion spiro, **1**, dans le benzène, conduit à une perte d'azote et à la formation d'un intermédiaire carbonyl-ylure. L'ylure se fragmente principalement en acétone et en 4-phényl-1,3-dioxane-2-ylidène que l'on peut piéger avec de l'alcool *tert*-butylique. En absence de piège, la voie réactionnelle principale suivie par le carbène en est une de fragmentation en biradical, le 5-phényl-2-oxa-1-oxopentane-1,5-diyle. Ce dernier radical peut se coupler à l'α-phényl-γ-butyrolactone et il se décarboxyle pour former du cyclopropylbenzène. Parmi les autres produits de la réaction, on a observé ceux résultant de l'insertion *apparente* du carbène dans une liaison C–H du benzène agissant comme solvant et dans une liaison C–H de l'acétone. De telles réactions ne semblent pas avoir été observées antérieurement et on propose des mécanismes alternatifs n'impliquant pas de carbène.

Mots clés : dioxacarbène, carbonyl-ylure, cyclopropylbenzène, biradical, lactone, oxadiazoline.

[Traduit par la Rédaction]

Introduction

Thermolysis of oxadiazolines (**1**) is now a well-established method for the generation of alkoxy- or dialkoxycarbenes (1). Fragmentation of alkoxy- or dialkoxycarbenes to radicals was reported many years ago, primarily for gas phase conditions (2), and computations for model systems followed (3). Such fragmentations of dialkoxycarbenes to radical pairs, in solution under relatively mild conditions, have recently been studied experimentally (4) and modeled (without solvation) with smaller analogues (3). Fragmentation of cyclic oxy- or dioxycarbenes to corresponding diradicals appears to be limited to a theoretical study by Borden and Hoo (5).

We now report the synthesis and thermolysis of oxadiazoline **1** in benzene at 110°C. The thermolysis occurs through a number of intermediates that are formed sequentially including a carbonyl ylide (**2**), a carbene (**3**), and diradicals **4** and **5** (Scheme 1).

Methods

Oxadiazoline **1** was synthesized by means of the sequence of reactions shown in Scheme 2. Ring opening of **6** was selective, leading primarily to **7**, which was saponified to **8**. The hydrazinolysis of **9** was also selective, affording primarily **10**, which crystallized from solution during the reaction. Oxidation of **11** with $Pb(OAc)_4$ led to a mixture of **1** and **12**. The intramolecular acid catalyzed substitution, leading from **12** to **1** to complete the cyclization, was modeled after intermolecular analogues (6).

A sample of **1** in benzene-d_6, in a sealed tube, was heated at 110°C for 72 h before an ^{1}H NMR spectrum of the crude mixture of products was acquired. The solvent and volatile products were then evaporated and the residue was chromatographed on SiO_2.

Results and discussion

Evidence for an ylide intermediate (**2**) came from the finding that a minor product was ketone **15** (Scheme 3). The yield of that product was not affected by inclusion of acetone (1.1 M) in the benzene solution of **1**, indicating that it could not have arisen from insertion of **3** into a C–H bond of acetone. Moreover, it could not have arisen from *any* reaction of free acetone.

We suggest that **15** arose from **2** through **13**, which came from a 1,4-sigmatropic H-shift in **2**. Such rearrangements of carbonyl ylides are known (7). Apparently, a fully concerted

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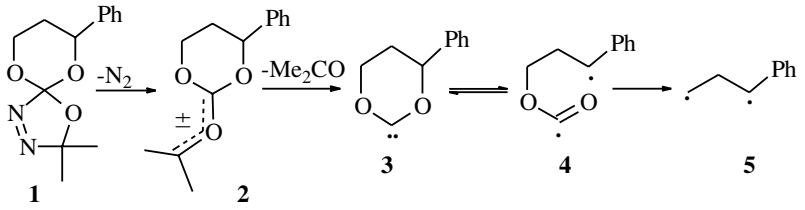
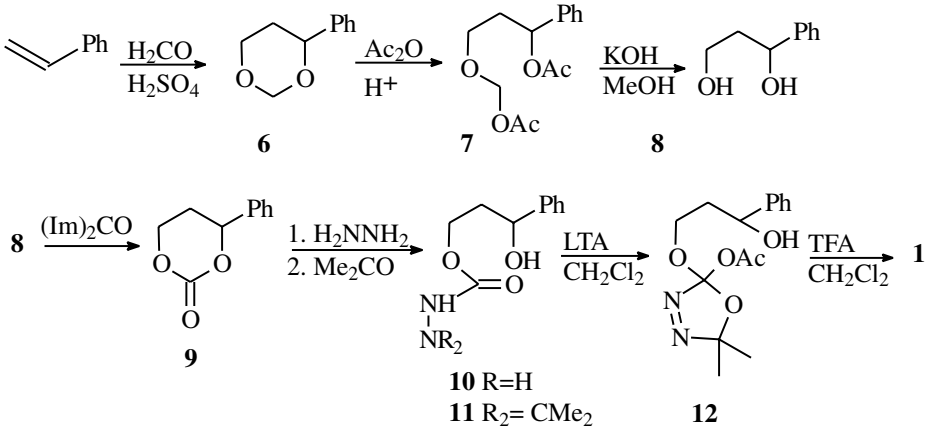
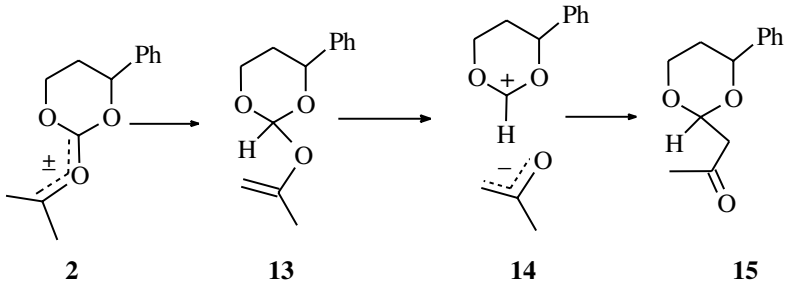
Scheme 1.



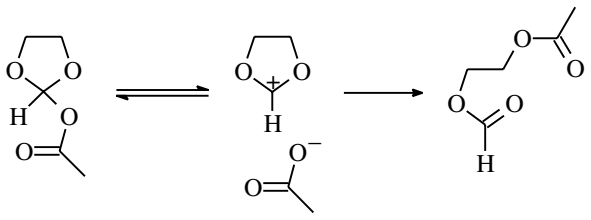
Scheme 2.



Scheme 3.



Scheme 4.

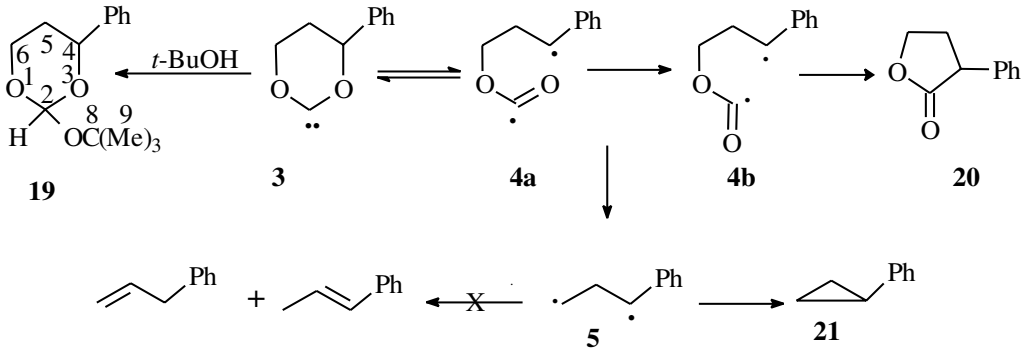


fragmentation of the oxadiazoline, to the carbene, N_2, and acetone, as suggested by Smith (8) on the basis of computation, is not general. Rearrangement of **13** to **15** is unprecedented, to the best of our knowledge, but it is reasonable, given that both fragments of ion pair **14** that are proposed for the rearrangement are stabilized. A good model system is the 2-acetoxy acetal **16**, thermolysis of which at 120°C affords the mixed diester **18** in 68% yield (9). The reaction can be understood in terms of reversible formation of an ion pair and nucleophilic substitution at carbon (Scheme 4). Return of the ion pair to **16** presumably scrambles the oxygen atoms of the acetoxy group whereas the enolate fragment in Scheme 3 would bond to carbon to form **15** irreversibly.

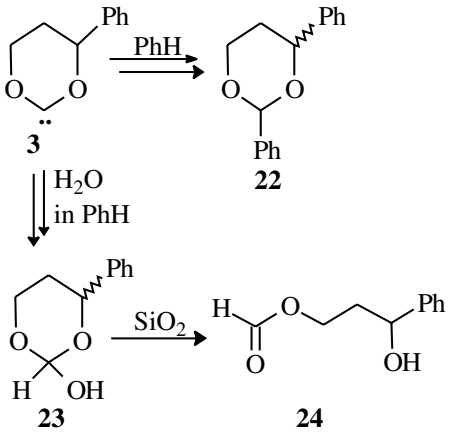
The formation of diastereomers **19** from thermolysis of **1** in benzene containing *tert*-butyl alcohol is evidence for carbene **3**, whereas the formation of lactone **20** and cyclopropylbenzene (**21**) in the absence of *tert*-butyl alcohol indicates that **3** fragments to diradical **4** (Scheme 5). There is analogy for the fragmentation of **3** to diradical **4** in the fragmentation of cinnamyloxy(methoxy)carbene to cinnamyl and methoxycarbonyl radicals and of benzyloxy(methoxy)carbene to benzyl and methoxycarbonyl radicals (4).

Cyclopropylbenzene (**21**) is an expected product from **5**, which is an intermediate from decarboxylation of **4**. We were unable to detect (by GC, with authentic samples for reference) either 1- or 3-propenylbenzene, which might also have arisen from **5** by means of intra- or intermolecular H-transfer. Reversal of **4** to **3** is speculative but, because **4** must be born with the geometry shown and because the barrier to radical coupling cannot be large, the reversal step (**4a**→**3**) is a probable, albeit invisible, reaction.

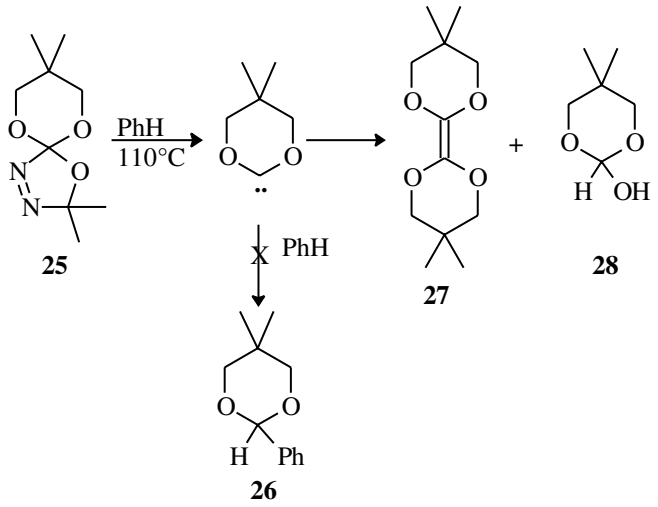
Scheme 5.



Scheme 6.



Scheme 7.

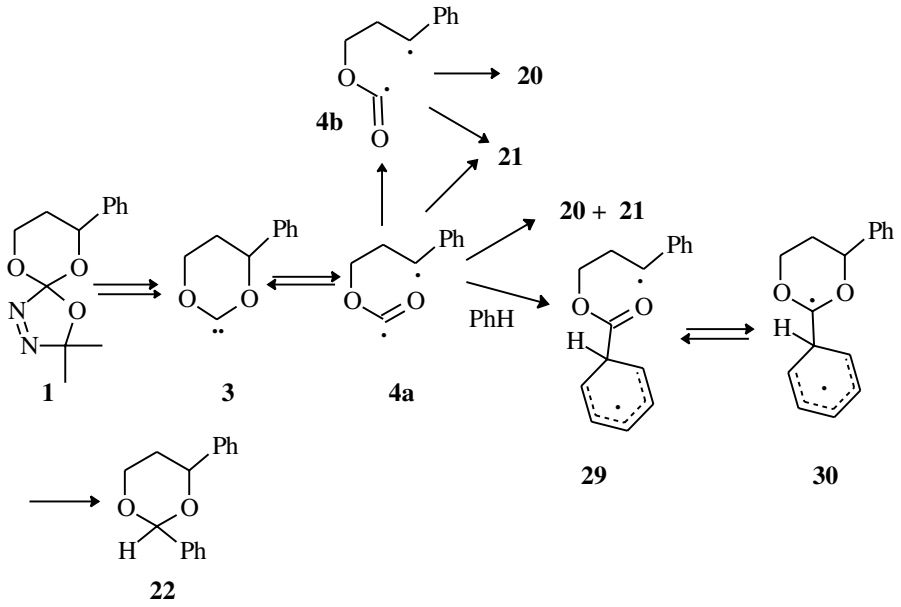


The formation of **20** and **21** in roughly equal amounts means that the rate constants for cyclization and decarboxylation of **4** at 110°C are very similar. The rate constant for decarboxylation was estimated as follows. From the Arrhenius equation of Newcomb (10) we obtained the rate constant k_H at 110°C for the reaction of RCH_2OCO radicals with $HSnBu_3$ ($k_H = 1.77 \times 10^6$ M^{-1} s^{-1}). The ratio k_H/k_{CO2} was available from the product ratio RCH_3:RCH_2OCHO = 38:25 for the reaction of RCH_2OCO radicals with $HSnBu_3$ (average concentration 0.025 M) in toluene at 110°C (11). Thus, the rate constant for decarboxylation came to $k_{CO2} \sim 6.8 \times 10^4$ s^{-1}, and the upper limit of the rate constant for cyclization of **4**, to form **20**, could be set at about 1×10^5 s^{-1}. That estimated rate constant is smaller than might have been expected, given that the process is an intramolecular coupling of a diradical to a five-membered ring. The reason for the small rate constant must lie in the fact that the initial conformation **4a** is the wrong one for coupling to **20**. Rotation into conformation **4b**, over a barrier of about 9 kcal mol^{-1}, is required (12) before lactone **20** can form. Such a barrier could limit the rate of coupling considerably, because the conformations **4a** and **4b** are only two of many conformations of the diradical. Rotations about the other single bonds of **4a** have barriers (13) smaller than 4 kcal mol^{-1} and therefore other conformations of the diradical will be populated before conformation **4b** is reached. Moreover, when **4b** is reached it will have only about a one-in-four chance of being in the singlet state (14). With these features in consideration, the relatively slow coupling of **4** to lactone **20** becomes understandable.

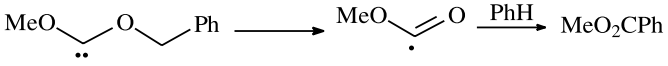
Additional products, not shown in the previous Schemes, were diastereomeric 2,4-diphenyl-1,3-dioxanes (**22**) (12) and diastereomeric hemiorthoformates (4-phenyl-1,3-dioxan-2-ols) (**23**). The latter products are readily accounted for in terms of capture of carbene **3** by adventitious water. Hemiorthoformates (**23**) were thermally stable, but an attempt at isolation by chromatography on silica led to 1-phenyl-1,3-propanediol-3-formate (**24**) (Scheme 6).

We were surprised to find **22** (12%, 6:1 ratio of diastereomers), because dialkoxycarbenes have never been shown to insert into a C–H bond of benzene. In fact, the more nucleophilic imidazolidene-2-ylidene does not appear to react with toluene, although products from apparent insertions into the acidic C–H bonds of acetylene and of a sulphone had been observed (15*a*). 1,3,4-Triphenyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene undergoes many reactions but not insertion into C–H bonds (15*b*). A possible reason for the apparently higher reactivity of **3**, relative to that of acyclic dialkoxycarbenes, was thought to be the enforced 0°, 0° conformation. For allyloxyhydroxycarbene, the 0°, 0° conformation was calculated to be 11.7 kcal mol^{-1} higher in energy than the most stable (180°, 180°) conformation (3*c*). A reduction of the stability of the carbene, as a result of raising the energy of the ground state, would reduce the barrier to insertion if the transition state for insertion were affected less, or not at all, by the conformational restriction. This attractive explanation was abandoned when it was found that

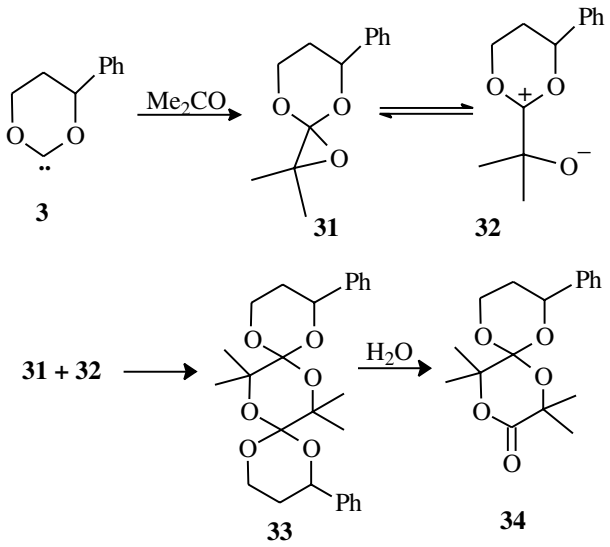
Scheme 8.



Scheme 9.



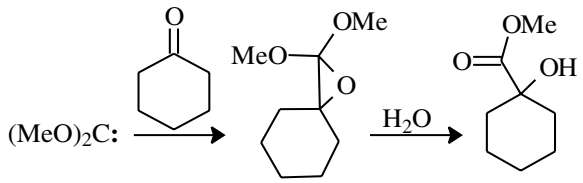
Scheme 10.



thermolysis of **25** in benzene (16) gave the carbene dimer **27** (20%) and 5,5-dimethyl-1,3-dioxan-2-ol (**28**, 21%), the latter being the result of reaction of the carbene with adventitious water (Scheme 7). There were additional products, but **26** could not be detected. With the results in Scheme 7, it is hard to ascribe **22** (Scheme 6) to insertion of **3** into benzene.

The only alternative mechanism that we could conceive of is radical substitution on benzene through the sequence of Scheme 8. Both intra- and intermolecular additions of acyl radicals to double bonds are known (17), as is radical aromatic substitution (18), and relatively slow closure of **4** (above) could permit aromatic substitution, via **29** and **30**, to

Scheme 11.

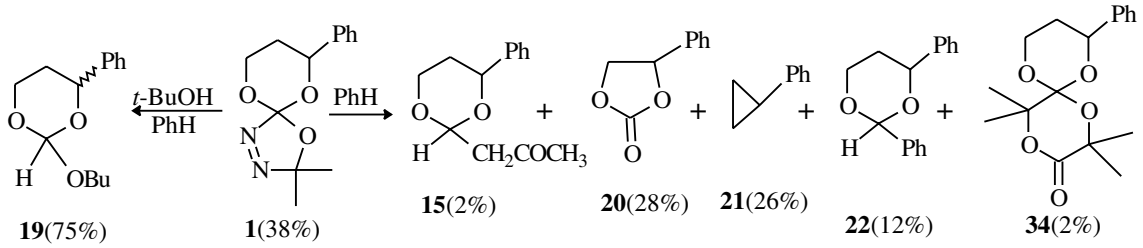


compete. The carbene from **25** does not fragment to a radical pair and attack on benzene was therefore not observed.

Having estimated the rate constant for decarboxylation and coupling, we were able to estimate the rate constant for attack on benzene by **4a** and (or) **4b** as follows. Knowing that the rates of coupling and decarboxylation are about twice as large as that of attack on benzene (from yields of the products) we could set $k_{CO_2} = 2k_{benzene}$[benzene]. The concentration of benzene is about 10 M and k_{CO_2} has an upper limit of 1×10^5 s^{-1} (above). Thus $k_{benzene}$ would not need to have a value greater than about 5×10^4 M^{-1} s^{-1} for aromatic substitution to compete. Aromatic substitution occurred when methoxycarbonyl radicals, generated in benzene by thermolysis of methyl azodicarboxylate at 130°C, gave methyl benzoate in 13% yield (19). Support for the postulate that aromatic substitution with **4** occurred also came from the discovery of methyl benzoate (3%) in the product mixture formed when benzyloxy(methoxy)carbene was generated in benzene (Scheme 9). We had not recognized that minor product previously (4*b*).

The cyclization step, **29→30**, is a 6-endo process for which there are now many examples, although we were unable to find a very close analogue (20). Subsequent formation of diastereomers **22** by a radical mechanism is not surprising, because kinetic control could apply in the migration step that forms the new C–H bond. There is ample precedent for the postulated H-migration in **30**. Analogous migrations from C-2 of 1,3-diyls are well known (21) although mono-radicals do not rearrange in that way. Synthesis

Scheme 12.



of authentic **22** by acid-catalyzed reaction of 1-phenyl-1,3-propanediol with benzaldehyde gave only one diastereomer, which we assume was the more stable *cis*-isomer, formed under thermodynamic control.

Spiro-fused ester **34** was also obtained, in 2% yield. The structure is not in doubt, but the source of it is not known. Addition of acetone (initial concentration 1.1 M) before thermolysis raised the yield of **34** to 28%! We have not developed an attractive explanation for its formation. A partial solution to the problem involves attack of the carbene (**3**) on acetone to afford **32**, which, like **2**, should be equilibrated with the oxirane **31** (Scheme 10). The postulated reaction of the carbene with acetone is in keeping with the observation that dimethoxycarbene reacts with cyclohexanone to afford an oxirane (22). Coupling of two units of **32** is unlikely, because **32** is a reactive intermediate that must be formed very slowly from **1**. However, a reaction between **31** and **32** is plausible, given that **31** is expected to be quite polar. Only two 2,2-dialkoxyoxiranes have been reported to date (22, 23) and they are sensitive materials that hydrolyse readily, as shown for one of them in Scheme 11. A bimolecular reaction between **31** and **32** would be expected to lead to **33**, and partial hydrolysis of **33** after the reaction tube was opened would yield the observed **34** (Scheme 10). Water in the added acetone cannot be a major contributor because the acetone was dried carefully and because the yield of hemiorthoformate (**23**) did not rise as a result of adding acetone to the benzene solvent prior to thermolysis.

In summary, the thermolysis chemistry of oxadiazoline **1** is exceptionally rich. It loses N_2 to form carbonyl ylide **2** that undergoes 1,4-sigmatropic rearrangement to afford **15** via **13**. The major fate of **2** is fragmentation to carbene **3** that can be trapped efficiently in a bimolecular reaction with *tert*-butyl alcohol. If **3** is not intercepted, it undergoes ring opening to diradical **4,** which undergoes three reactions at comparable rates. The diradical attacks benzene through a sequence of unprecedented reactions that lead to substitution product **22**. Diyl **4** also cyclizes to lactone **20** and it decarboxylates to afford phenylcyclopropane via cyclization of diyl **5**. Finally, the formation of **34** suggests that oxirane **31** is an undetected intermediate from the reaction of **3** with acetone. The products, accounted for individually above, are listed in Scheme 12.

Experimental

General

NMR spectra were collected with Bruker AV-300 or AV-500 NMR spectrometers, with samples in $CDCl_3$. The chemical shifts, in ppm, are referenced to the ^1H signal from residual $CHCl_3$ at 7.26 ppm or to the ^{13}C signal at 77.0 ppm. The coupling constants of the first-order multiplets are in Hz. Chemical shift assignments are based on analysis of ^1H–^1H COSY, ^1H–^{13}C HSQC, and ^1H–^{13}C HMBC spectra. Connectivities of the atoms were determined with the aid of both ^1H–^{13}C HMBC and ^1H–^{13}C HSQC 2-D NMR experiments. Assignments of signals to axial (ax) and equatorial (eq) ^1H atoms are based on good analogy (24).

4-Phenyl-1,3-dioxane (6) (25)

Styrene (100 g, 0.96 mol) was dissolved in 200 mL (2.5 mol) of 37% formaldehyde. Concentrated H_2SO_4 (8.0 mL, 0.14 mol) was added, the round-bottom flask was fitted with a reflux condenser, and the mixture was refluxed for 7 h. After cooling, the solution was washed twice with 160 mL of benzene and the combined benzene layers were washed twice with 250 mL of water. Most of the benzene was removed by distillation (80°C) at atmospheric pressure. The pressure was then reduced to 2 mm Hg (1 mm Hg = 133.322 Pa), and 4-phenyl-1,3-dioxane was collected as a clear oil (83.9 g, 0.51 mol, 57%), boiling between 96 and 130°C. ^1H NMR (200 MHz, $CDCl_3$) δ: 1.71 (m, 1H), 2.10 (ddd, ^3J = 4.9 Hz, ^3J = 12.2 Hz, ^3J = 12.4 Hz, ^2J = 12.4 Hz, 1H), 3.87 (ddd, ^3J = 2.5 Hz, ^3J = 11.8 Hz, ^2J = 11.8 Hz, 1H), 4.19 (dd, ^3J = 4.8 Hz, ^2J = 11.4 Hz, 1H), 4.64 (dd, ^3J = 2.5 Hz, ^2J = 11.2 Hz, 1H), 4.89 (d, ^2J = 6.3 Hz, 1H), 5.22 (d, ^2J = 6.3 Hz, 1H), 7.26–7.39 (m, 5H).

1,5-Diacetoxy-5-phenyl-2-oxapentane (7) (26)

Concentrated HCl (1 mL) was added to 4-phenyl-1,3-dioxane (**6**) (80 g, 0.49 mol) dissolved in acetic anhydride (138 mL, 1.46 mol) and the solution was heated to 80°C for 20 h. The solution was cooled, neutralized with 10% NaOH to pH 7 (as determined with universal litmus paper), and then washed twice with ether (50 mL). The ether layer was dried with magnesium sulfate. After vacuum filtration the ether was removed with a rotary evaporator leaving **7** (108.4 g, 0.41 mol, 83%) as an orange oil. ^1H NMR (500 MHz, $CDCl_3$) δ: 1.87 (s, 3H), 1.90–1.96 (m, 1H), 1.99 (s, 3H), 2.05–2.12 (m, 1H), 4.01–4.06 (m, 1H), 4.13–4.18 (m, 1H), 4.65 (m, 1H), 5.01 (d, ^3J = 2.6 Hz, 1H), 5.28 (d, ^3J = 2.6 Hz, 1H), 7.24–7.32 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.49, 20.60, 36.70, 60.80, 78.01, 86.81, 126.36, 127.82, 128.35, 140.81, 170.17, 170.58. EI-MS *m/z*: 206 (1), 177 (4), 163 (3), 146 (17), 133 (6), 117 (29), 107 (25), 91 (6), 77 (8), 43 (100). CI-MS (NH_3) *m/z*: 284 ($[M + NH_4]^+$, 28), 177 (100), 146 (17), 117 (95), 75 (4).

1-Phenyl-1,3-propanediol (8) (27)

To a solution of **7** (15.62 g, 0.058 mol) in 10 mL of ether was slowly added a saturated solution of KOH in methanol

(30 mL). The solution was stirred for 3 h before it was neutralized with 5% HCl. The aqueous–methanol layer was extracted twice with 30 mL of ether. Evaporation of most of the ether and subsequent distillation of the residue gave 1-phenyl-1,3-propanediol (4.7 g, 0.031 mol, 54%), boiling at 119°C, 0.5 mm Hg (1 mm Hg = 133.322 Pa) (lit. (28) value bp 117 to 118°C at 0.25 mm Hg). ^{1}H NMR (200 MHz, CD_3OD) δ: 1.68–1.91 (m, 2H), 3.62–3.41 (m, 2H), 4.83 (dd, ^3J = 2.6 Hz, ^3J = 5.4 Hz, 1H), 7.22–7.52 (m, 5H). ^{13}C NMR (50 MHz, CD_3OD) δ: 42.71, 65.50, 75.92, 126.73, 128.20, 129.40, 146.33. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.86 (m, 2H), 3.76 (m, 2H), 4.83 (dd, ^3J = 4.7 Hz, ^3J = 7.9 Hz, 1H), 7.22–7.52 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 40.34, 60.44, 73.08, 125.55, 127.25, 128.25, 144.19. EI-MS *m/z*: 152 ([M]$^+$, 14), 133 (9), 105 (50), 107 (100), 91 (16), 79 (78), 51 (23), 43 (16). CI-MS (NH_3) *m/z*: 170 ([M + NH_4]$^+$, 21), 152 (100), 135 (56), 117 (86), 91 (16).

4-Phenyl-1,3-dioxan-2-one (9) (29)

1,1′-Carbonyldiimidazole (3.51 g, 0.022 mol) in 100 mL of dichloromethane was added dropwise (ca. 1 h) to a solution of **8** (3.0 g, 0.02 mol) and pyridine (4.4 mL, 0.054 mol) in 180 mL of dichloromethane. After stirring overnight the solution was washed three times with 5% HCl (250 mL), and once each with water (250 mL) and brine (250 mL). The dichloromethane layer was dried with $MgSO_4$ and, after filtration, the solvent was removed with a rotary evaporator to leave **9** as white crystals (2.49 g, 0.014 mol, 70%) after recrystallization from hot ethanol; mp 53–54°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.20–2.38 (m, 2H), 4.46–4.51 (m, 2H), 5.51 (dd, ^3J = 3.8 Hz, ^3J = 9.6 Hz, 1H), 7.26–7.44 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 29.42, 66.87, 80.15, 125.67, 127.83, 129.0 137.90, 148.77 (C=O). EI-MS *m/z*: 178 ([M]$^+$, 12), 117 (82), 104 (100), 91 (11), 77 (51), 56 (48), 51 (36). CI-MS (NH_3) *m/z*: 196 ([M + NH_4]$^+$, 100), 179 ([M + H]$^+$, 30), 134 (9), 117 (89), 104 (8). HR-MS calcd. for $C_{10}H_{10}O_3$: 178.0629; found: 178.0657.

Synthesis of 10 by hydrazinolysis of 9

Hydrazine monohydrate (7.1 mL, 0.15 mol) was added, with stirring, to 4-phenyl-1,3-dioxan-2-one (**9**) (3.96 g, 0.022 mol) in 70 mL of dichloromethane under nitrogen. In about 2 h a white precipitate had formed. The heterogeneous mixture was filtered leaving the product as white crystals (3.63 g, 0.017 mol, 77%). ^{1}H NMR (200 MHz, CD_3OD) δ: 1.92 (m, 2H), 4.00–4.12 (m, 2H), 4.66 (m, 1H), 7.17–7.26 (m, 5H). ^{13}C NMR (50 MHz, CD_3OD) δ: 39.50, 63.39, 71.73, 126.93, 128.38, 129.38, 145.96, 160.69 (C=O). EI-MS *m/z*: 211 ([M + H]$^+$, 1), 192 (7), 134 (9), 118 (11), 117 (100), 91 (11), 79 (16), 57 (11), 43 (12). CI-MS (NH_3) *m/z*: 211 ([M + H]$^+$, 3), 193 (100), 152 (13), 135 (8), 117 (100), 105 (8), 76 (11), 69 (19), 43 (52).

3-Isopropylidene carbazic acid 3-hydroxy-3-phenylpropyl ester (11)

To a solution of **10** (1.10 g, 5.23 mmol) in dichloromethane (10 mL) was added 1 mL of acetone. After the **10** had dissolved, Na_2SO_4 (0.24 g, 1.4 mmol) was added, and the mixture was stirred for 2 h. The Na_2SO_4 was removed by filtration and the solvent was removed with a rotary evaporator. Compound **11** was obtained as a white solid (0.78 g, 3.1 mmol, 60%); mp 109–110°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.82 (s, 3H), 2.03 (s, 3H), 2.07–2.11 (m, 2H), 4.24–4.27 (m, 1H), 4.45–4.53 (m, 1H), 4.81 (dd, ^3J = 4.2 Hz, ^3J = 4.5 Hz, 1H), 7.27–7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 16.24, 25.49, 38.62, 63.30, 71.36, 125.89, 127.69, 128.64, 144.10, 151.37, 154.45. EI-MS *m/z*: 251 ([M + H]$^+$, 1), 144 (15), 117 (100), 91 (17), 72 (38), 56 (31), 43 (38). CI-MS (NH_3) *m/z*: 251 ([M + H]$^+$, 29), 233 (23), 193 (48), 117 (100), 99 (12), 72 (19). HR-MS calcd. for $C_{13}H_{19}N_2O_3$: 251.1395; found: 251.1382.

3,4-Diaza-2,2-dimethyl-7-phenyl-1,6,10-trioxaspiro[5.4]dec-3-ene (1)

To an ice-cooled solution of lead(IV) acetate (4.43 g, 0.010 mol) in dichloromethane (25 mL) under nitrogen was added, dropwise, over a period of 1 h, a solution of **11** (1 g, 0.004 mol) in dichloromethane (5 mL). After addition, stirring was continued for 2 days. The solution was filtered through Celite, washed four times with 25 mL of 5% $NaHCO_3$ solution and dried over Na_2SO_4. ^{1}H NMR spectroscopy of an aliquot indicated that the product was probably a mixture of **1** and **12**. The solvent was evaporated and the residue was dissolved in dichloromethane (20 mL) before trifluoroacetic acid (0.01 mL) was added. After 90 min the cyclization of **12** to **1**, monitored with TLC, was complete. The solution was washed with aqueous NaOH and dried over $MgSO_4$. Evaporation of the solvent and radial chromatography of the residue (Chromatotron, 10% EtOAc – hexanes) gave **1**, a white solid, as a mixture of two diastereomers in 1:1 ratio (0.38 g, 1.5 mmol, 38%). ^{1}H NMR (composite spectrum, 300 MHz, $CDCl_3$) δ: 1.48 (s, 3H), 1.52 (s, 3H), 1.53 (s, 6H), 1.90–2.03 (m, 2H), 2.18–2.39 (m, 2H), 4.23–4.31 (m, 2H), 4.35 (ddd, ^3J = 3.5 Hz, ^3J = 11.3 Hz, ^2J = 11.3 Hz, 1H) 4.81 (ddd, ^3J = 2.8 Hz, ^3J = 11.8 Hz, ^2J = 11.9 Hz, 1H), 5.24 (dd, ^3J = 3.1 Hz, ^3J = 11.6 Hz, 1H), 5.73 (dd, ^3J = 2.7 Hz, ^3J = 11.6 Hz, 1H), 7.23–7.40 (m, 10H). ^{13}C NMR (composite spectrum, 75 MHz, $CDCl_3$) δ: 24.49, 24.64, 31.74, 31.92, 63.02, 65.16, 74.62, 77.09, 119.81, 120.44, 125.92, 128.18, 128.54, 140.21 (analogous, but not spirocyclic, oxadiazolines typically have a C-5 signal at δ 118.7–119.4 and a C-2 signal at δ 136.7–137.9) (30). EI-MS *m/z*: 162 ([M–N_2–Me_2CO]$^+$, 1), 116 (72), 117 (100), 104 (12), 91 (19), 65 (3), 43 (19).

Thermolysis of 1 in the presence of *tert*-butyl alcohol

A solution of oxadiazoline **1** (27.4 mg, 0.11 mmol) and *tert*-butyl alcohol (82.2 mg, 1.1 mmol) in 2 mL of benzene was flame sealed into an NMR tube. The tube was heated for 72 h at 110°C with a constant-temperature oil bath. Two diastereomers of 2-*tert*-butoxy-4-phenyl-1,3-dioxane (**19**) (75% combined yield) were obtained in a ratio of 3:1, as determined by integration of clean singlets at δ 5.64 and 6.03. The crude sample was not purified but the signals corresponding to the major diastereomer could be assigned. Some integrations are approximate, because of partial overlap with signals from the minor diastereomer.

^{1}H NMR (major diastereomer, 500 MHz, C_6D_6) δ: 1.59 (s, 9H, CH_3), 1.48–1.73 (dm, 1H, H5-eq), 1.96 (ddd, ^3J = 5.0 Hz, ^3J = 12.6 Hz, ^3J = 12.4 Hz, ^2J = 12.4 Hz, 1H, H5-ax), 3.36–3.50 (m, 1H, H6-ax), 3.57 (dd, ^3J = 1.4 Hz, ^3J = 4.0 Hz, ^2J = 11.0 Hz, 1H, H6-eq), 5.32 (dd, ^3J =

2.4 Hz, ^3J = 11.7 Hz, 1H, H4-ax), 6.03 (s, 1H), 7.03–7.37 (m, 5H). ^{13}C NMR (125 MHz, C_6D_6) δ: 28.74 (C9), 33.77 (C5), 58.32 (C6), 69.44 (C4), 77.13 (C8), 105.21 (C2), 125.91, 128.08, 128.32, 142.90. EI-MS *m/z*: 152 (6), 134 (31), 107 (100), 79 (84), 59 (14), 51 (30). CI-MS (NH_3) *m/z*: 196 (8), 179 (8), 152 (24), 134 (17), 117 (100), 105 (19).

Thermolysis of 1 in benzene

Oxadiazoline **1** (0.1515 g, 0.61 mmol), and the internal standard 1,4-dimethoxybenzene (0.0205 g, 0.148 mmol) were dissolved in 6 mL of benzene and sealed into a thermolysis tube after three cycles of freeze-pump-thaw degassing. The tube was then kept in an oil bath at 110°C for 72 h. The crude mixture of products was injected into the GC–FID to determine the product yields. The peak areas were corrected for the detector response and products were identified by coinjection of authentic compounds. The remainder of the mixture was freed from solvent and the residue was separated by radial chromatography (Chromatotron, 100% hexanes) to afford the following products.

*Cyclopropylbenzene (**21**) (31)*

26%. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.85 (m, 2H), 1.11 (m, 2H), 2.02 (m, 1H), 7.19–7.43 (m, 5H). EI-MS *m/z*: 118 ($[M]^+$, 54), 117 (100), 115 (48), 91 (74), 77 (22).

*4-Phenyl-1,3-dioxan-2-one (**9**) (29)*

5%.

*α-Phenyl-γ-butyrolactone (**20**) (32, 33)*

28%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.40 (dddd, ^3J = 8.2, 9.2, 10.1 Hz, ^2J = 12.6 Hz, 1H), 2.71 (dddd, ^3J = 3.4, 6.8, 9.1 Hz, ^2J = 12.6 Hz, 1H), 3.80 (dd, ^3J = 9.7 Hz, ^3J = 9.9 Hz, 1H), 4.34 (ddd, ^3J = 6.7, 9.1 Hz, ^2J = 9.1 Hz, 1H), 4.46 (ddd, ^3J = 3.4, 8.2 Hz, ^2J = 9.1 Hz, 1H), 7.27–7.40 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.62, 45.54, 66.56, 127.71, 127.98, 129.00, 136.79, 177.43. EI-MS *m/z*: 162 ($[M]^+$, 22), 117 (100), 103 (16), 91 (48), 77 (24), 63 (14), 51 (15). HR-MS calcd. for $C_{10}H_{10}O_2$: 162.0681; found: 162.0675.

*4-Phenyl-1,3-dioxan-2-ol (**23**)*

19% (not isolable, structure assignment tentative, diastereomer ratio not known). EI-MS *m/z*: 163 ($[M - OH]^+$, 1), 133 (2), 117 (100), 105 (30), 91 (20), 77 (39).

*1-Phenyl-1,3-propanediol-3-formate (**24**) (34)*

^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.02–2.19 (m, 2H), 4.23 (ddd, ^3J = 5.9 Hz, ^3J = 5.7 Hz, ^3J = 5.7 Hz, ^2J = 11.3 Hz, 1H), 4.43 (ddd, ^3J = 5.9 Hz, ^3J = 5.7 Hz, ^3J = 5.7 Hz, ^2J = 11.3 Hz, 1H), 4.83 (dd, ^3J = 5 Hz, ^3J = 7.6 Hz, 1H), 7.35–7.36 (m, 5H), 8.08 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 37.93, 61.27, 71.31, 125.85, 128.04, 128.80, 143.90, 161.22. EI-MS *m/z*: 180 ($[M]^+$, 3), 163 (4), 152 (7), 134 (52), 107 (96), 91 (20), 79 (100), 51 (21), 43 (17). HR-MS calcd. for $C_{10}H_{12}O_3$: 180.0786; found: 180.0778.

*1-(4-Phenyl-1,3-dioxan-2-yl)-2-propanone (**15**)*

2%. Apparently only one diastereomer was isolated. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.70 (ddd, ^3J = 2.5 Hz, ^3J = 3.5 Hz, ^2J = –13.4 Hz, 1H, H5-eq), 1.99 (dddd, ^3J = 4.6 Hz, ^2J = –13.3 Hz, ^3J = 11.9 Hz, ^3J = 11.9 Hz, 1H, H5-ax), 2.22 (s, 3H), 2.84 (d, ^3J = 5.1 Hz, 2H), 3.94 (ddd, ^3J = 2.6 Hz, ^3J = 11.7 Hz, ^2J = –11.9 Hz, 1H, H6-ax), 4.20 (ddd, ^3J = 1.3 Hz, ^3J = 4.9 Hz, ^2J = –11.5 Hz, 1H, H6-eq), 4.72 (dd, ^3J = 2.5 Hz, ^3J = 11.4 Hz, 1H, H4-ax), 5.17 (t, ^3J = 5.1 Hz, 1H, H2), 7.28–7.4 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 31.51, 33.17, 49.33, 67.02, 78.93, 99.06, 125.95, 127.98, 128.61, 141.49, 205.21. CI-MS (NH_3) *m/z*: 238 ($[M + NH_4]^+$, 25), 221 ($[M + H]^+$, 58), 187 (31), 152 (30), 135 (44), 117 (100), 91 (14), 78 (10), 43 (14).

*8,8,11,11-Tetramethyl-2-phenyl-1,5,7,10-tetraoxa-9-oxospiro[5.5]undecane (**34**)*

2%. Connectivity determined by means of ROESY 2-D NMR spectroscopy. IR (NaBr, neat) (cm^{-1}): 1739. ^{1}H NMR (500 MHz, C_6D_6) δ: 1.15 (dddd, ^3J = 1.5, 2.6, 2.6 Hz, ^2J = 13.4 Hz, 1H, H3-eq), 1.48 (s, 3H, H11′), 1.50 (s, 3H, H11″), 1.53 (s, 3H, H8′), 1.56 (s, 3H, H8″), 1.62 (dddd, ^3J = 4.9, 11.7, 12.9 Hz, ^2J = 13.1 Hz, 1H, H3-ax), 3.41 (ddd, ^3J = 1.6, 4.9 Hz, ^2J = 11.1 Hz, 1H, H4-eq), 3.97 (ddd, ^3J = 2.5, 12.8 Hz, ^2J = 11.1 Hz, 1H, H4-ax), 5.00 (dd, ^3J = 2.7, 11.7 Hz, 1H, H10-ax), 7.08–7.12 (m, 5H). ^{13}C NMR (125 MHz, C_6D_6) δ: 24.07 (C11′), 24.20 (C11′), 28.58 (C8′), 28.72 (C8′), 32.47 (C3), 60.34 (C4), 71.65 (C2), 76.74 (C11), 84.16 (C8), 109.07 (C6), 128.85, 128.39, 128.15, 141.42, 171.06 (C=O). EI-MS *m/z*: 204 (4), 179 (4), 117 (100), 104 (18), 70 (70), 43 (37). CI-MS (NH_3) *m/z*: 307 ($[M + H]^+$, 18), 134 (18), 117 (100), 70 (32). The yield of this product rose to 28% in an experiment in which the starting solvent was 1.1 M in acetone.

*2,4-Diphenyl-1,3-dioxane (**22**)*

12%. Diastereomers in 6:1 ratio (by NMR, after chromatography, which failed to separate them and may have altered the initial diastereomer ratio). ^{1}H NMR (major diastereomer, 500 MHz, $CDCl_3$) δ: 1.81 (ddd, ^3J = 2.5, 4.0 Hz, ^2J = 13.4 Hz, 1H, H5-eq), 2.14 (dddd, ^3J = 4.9, 12.2, 11.9 Hz, ^2J = 13.4 Hz, 1H, H5-ax), 4.14 (ddd, ^3J = 2.5, 11.9 Hz, ^2J = 11.9 Hz, 1H, H6-ax), 4.37 (ddd, ^3J = 1.3, 4.9 Hz, ^2J = 11.5 Hz, 1H, H6-eq), 4.92 (dd, ^3J = 2.6, 11.4 Hz, H4-ax), 5.73 (s, 1H, H2-ax), 7.28–7.58 (m, 10H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 33.63 (C5), 67.48 (C6), 79.29 (C4), 101.79 (C2), 126.03, 126.38, 127.89, 128.38, 128.59, 128.95, 131.04, 138.88, 141.86. EI-MS *m/z*: 239 ($[M - H]^+$, 1), 134 (7), 117 (61), 105 (100), 78 (35), 77 (82), 51 (32). CI-MS (NH_3) *m/z*: 241 ($[M + H]^+$, 24), 152 (16), 134 (40), 117 (100), 91 (24). The minor diastereomer was inferred from the presence of a singlet at 5.23 ppm, upfield from that of the major diastereomer by 0.55 ppm. In the two diastereomers formed from trapping of the carbene with *tert*-butyl alcohol the minor diastereomer gave rise to a singlet 0.39 ppm upfield from the signal for the orthoformyl H of the major diastereomer.

Thermolysis of 1 in the presence of added acetone

A solution of oxadiazoline **1** (0.1684 g, 0.679 mmol) and acetone (0.5 mL) in benzene (5.5 mL) was sealed into a thermolysis tube after three cycles of freeze–pump–thaw degassing. The tube was kept in an oil bath at 110°C for 72 h. After thermolysis the internal standard, 1,4-dimethoxybenzene (6.8 mg, 0.1218 mmol), was added and the crude solution was injected into the GC–FID for determination of product yields. Detector response factors were applied to obtain the corrected yields below.

Cyclopropylbenzene (**21**) (4%), α-phenyl-γ-butyrolactone (**20**) (5%), 2-hydroxy-4-phenyl-1,3-dioxane (**23**) (21%), 1-(4-phenyl-1,3-dioxan-2-yl)-2-propanone (**15**) (2%), 8,8,11,11-tetramethyl-2-phenyl-1,5,7,10-tetraoxa-9-oxospiro[5.5]undecane (**34**) (28%), 2,4-diphenyl-1,3-dioxane (diastereomers) (**22**) (13%), 4-phenyl-1,3-dioxan-2-one (**9**) (7%).

Synthesis of *cis*-2,4-diphenyl-1,3-dioxane

The procedure was modeled after one (35) for making an analogue. To 1-phenyl-1,3-propanediol (5 g, 0.032 mol) and benzaldehyde (3.4 g, 0.036 mol) in dichloromethane (50 mL) was added *p*-toluenesulfonic acid (0.5 g, 2.9 mmol). The solution was stirred overnight before it was washed with 10 mL of $NaHCO_3$ and dried over Na_2SO_4. The residue obtained upon removal of the solvent was purified by means of column chromatography (10% EtOAc – hexanes) yielding **22** (5.65 g, 73%). The *cis* configuration was assigned on the basis of the known preference for the C-2 phenyl group to be in the equatorial position (36). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.83 (m, 1H, H5-eq), 2.18 (dddd, ^3J = 4.9, 12.2, 12.2 Hz, ^2J = 12.3 Hz, 1H, H5-ax), 4.16 (ddd, ^3J = 2.3, 11.8 Hz, ^2J = 11.8 Hz, 1H, H6-ax), 4.40 (ddd, ^3J = 1.0, 4.5 Hz, ^2J = 11.4 Hz, 1H, H6-eq), 4.98 (dd, ^3J = 2.4, 11.2 Hz, 1H, H4-ax), 5.73 (s, 1H, H2), 7.33–7.66 (m, 10H).

3,4-Diaza-2,2,8,8-tetramethyl-1,6,10-trioxaspiro[5.4]dec-3-ene (25)

The synthesis and properties of **25** have been described (16).

5,5-Dimethyl-1,3-dioxan-2-ol (28)

Unstable material, isolated in 21% yield by preparative GC (OV-17, 6′ × 1/4″, He at 40 mL min^{-1}) and tentatively identified as **28**. ^{1}H NMR (200 MHz, C_6D_6) δ: 1.02 (s, 3H), 1.76 (s, 3H), 3.13 (d, ^2J = 10.6 Hz, 2H), 3.81 (d, ^2J = 10.6 Hz, 2H), 5.97 (s, 1H).

Carbene dimer (27)

Yield 20%, isolated by preparative GC (conditions above). ^{1}H NMR (300 MHz, C_6D_6) δ: 0.067 (s, 12H), 3.43 (s, 8H). ^{13}C NMR (75 MHz, C_6D_6) δ: 21.86, 30.95, 78.36, 136.69. EI-MS *m/z*: 229 ([M + H]$^+$, 4), 191 (8), 161 (13), 132 (32), 115 (92), 69 (100), 56 (78). HR-MS calcd. for $C_{12}H_{21}O_4$ [M + H]$^+$: 229.1439; found: 229.1453.

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