Benzyloxy(4-substituted benzyloxy)carbenes. Generation from oxadiazolines and fragmentation to radical pairs in solution

Nadine Merkley and John Warkentin

Abstract: Thermolysis of 2,2-dibenzyloxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazoline in benzene at 110°C leads to dibenzyloxycarbene. The carbene was trapped with *tert*-butyl alcohol to afford dibenzyl-*tert*-butyl orthoformate. In the absence of a trapping agent for the carbene, it fragmented to benzyloxycarbonyl and benzyl radicals, as shown by trapping the latter with TEMPO. In the absence of both TEMPO and *tert*-butyl alcohol, the radicals were partitioned between coupling to benzyl phenylacetate and decarboxylation, with subsequent formation of bibenzyl. The preferred sense of fragmentation of the analogous carbenes from benzyloxy-(*p*-substituted-benzyloxy)carbenes was determined by comparing the yields of the two possible esters, $ArCH_2O(CO)CH_2Ph$ and $PhCH_2O(CO)CH_2Ar$. It was found that an electron-withdrawing group in the *para* position favoured fragmentation to the benzylic radical containing that group. A Hammett plot of the data gave a best fit with σ^- substituent constants (r = 0.994, $\rho_{(PhH,\ 110°C)}$ = 0.7) suggesting that the fragmentation involves charge separation in the sense that increases electron density on the group that is becoming a benzylic radical and decreases electron density on the carbonyl group that is becoming the benzyloxycarbonyl radical.

Key words: carbene, dibenzyloxycarbene, fragmentation, substituent effect, radical pair, TEMPO.

Résumé : La thermolyse du 2,2-dibenzyloxy-5,5-diméthyl-Δ^3-1,3,4-oxadiazoline, dans le benzène à 100°C, conduit à la formation de dibenzyloxycarbène. On a piégé le carbène à l'aide d'alcool *tert*-butylique, avec formation d'orthoformiate de dibenzyle et de *tert*-butyle. En absence d'agent pour piéger le carbène, il se fragmente pour conduire à la formation de radicaux benzyloxycarbonyle et benzyle dont l'existence à été démontrée en piégeant le dernier à l'aide de « TEMPO ». En absence d'alcool *tert*-butylique ainsi que de « TEMPO », les radicaux se répartissent entre un couplage conduisant au phénylacétate de benzyle et une décarboxylation avec formation subséquente de dibenzyle. En se basant sur une comparaison des rendements des deux esters possibles, $ArCH_2O(CO)CH_2Ph$ et $PhCH_2O(CO)CH_2Ar$, on a déterminé la voie préférée de fragmentation de carbènes analogues provenant de carbènes portant des groupes benzyloxyles différents, l'un substitué en para et l'autre non substitué. On a trouvé qu'un groupe électroaffinitaire en position para favorise la fragmentation conduisant aux radical benzylique contenant ce groupe. Le meilleur ajustement de la courbe d'Hammett des données est obtenu avec des constantes de substituants σ^- (r = 0,994, $\rho_{(PhH,\ 110°C)}$ = 0,7), ce qui suggère que l'état de transition pour la fragmentation implique une séparation de charge dans le sens qui augmente la densité électronique sur le groupe qui devient un radical benzylique et qui diminue la densité électronique sur le groupe carbonyle qui devient le radical benzyloxycarbonyle.

Mots clés : carbène, dibenzyloxycarbène, fragmentation, effet de substituant, paire de radicaux, « TEMPO ».

[Traduit par la Rédaction]

Introduction

Most reactions of carbenes increase the co-ordination number of the carbene carbon from two to four, as expected for a species having a pair of electrons in a σ–orbital and a virtual *p*-orbital (singlet) or an unpaired electron in each of two singly occupied orbitals (triplet). It may be surprising that stabilized carbenes can break a bond to the carbene carbon, instead of forming new ones, but such a fragmentation has been observed with oxycarbenes and dioxycarbenes. Presumably it is the formation of the strong carbonyl double bond that drives those fragmentations, which can be heterolytic or homolytic. Heterolytic fragmentations, to ion pairs, have been reported when alkoxy(halo)carbenes are generated in a polar solvent such as acetonitrile, Scheme 1 (1–5). Homolytic fragmentations of dioxycarbenes can occur in the gas phase or in non-polar solvents, particularly if one of the oxy groups is allylic or benzylic, Scheme 1 (6–10).

Recently it was reported that methoxy(cinnamyloxy)carbene and its isomer, generated by thermolysis of oxadiazolines **1a** and **1b** in benzene at 110°C (10) fragment to radical pairs. The carbene from **1a** could be trapped with *tert*-butyl alcohol and the radicals could be trapped with TEMPO. Moreover, the sequence oxadiazoline → carbene → radical pair was supported, Scheme 2, by showing that the yield of orthoformate increased, at the expense of esters, with

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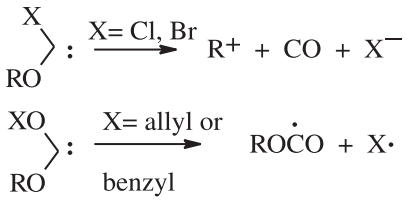
N. Merkley and J. Warkentin.[1] Department of Chemistry, McMaster University, Hamilton, ON L8S 4M1, Canada.

[1]Author to whom correspondence may be addressed. Fax: (905) 522-2509. e-mail: warkent@mcmaster.ca

Scheme 1.

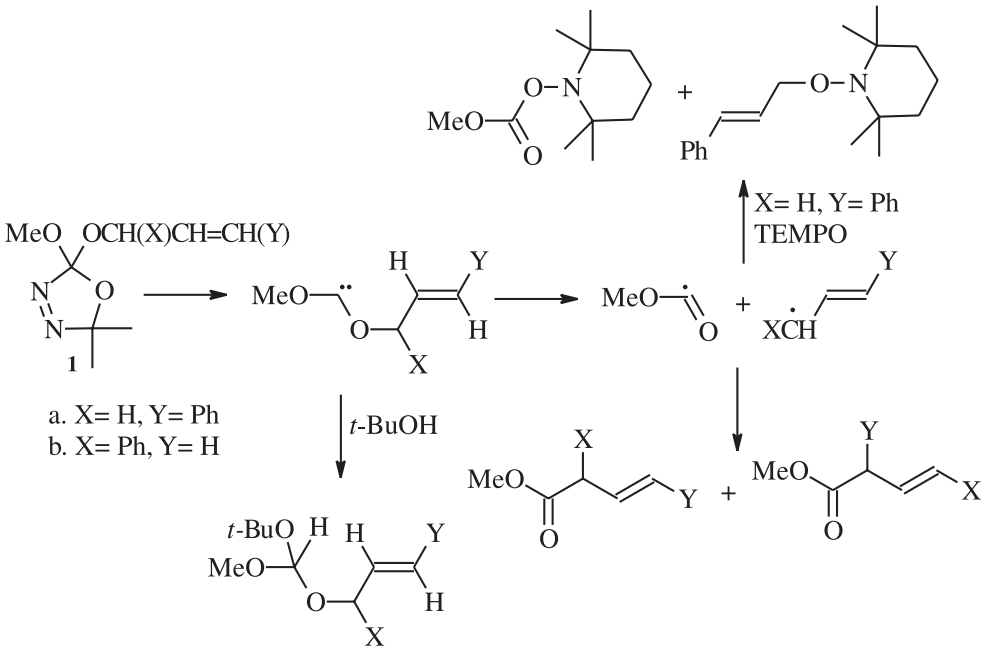


increasing concentration of carbene trap. More recently benzyloxymethoxycarbene was shown to fragment similarly, to methoxycarbonyl and benzyl radicals, and again both the carbene and the radicals were trapped (11). Although *p*-substituted benzyloxy oxadiazolines were studied also, it was not possible to make strong inferences about the effects of *p*-substituents on the ease of carbene fragmentation from the yields of esters, which were below 50%. In those circumstances a dependence of yields on substituents could possibly be attributed to a substituent effect on a competing reaction, such as the observed alternative fragmentation of the oxadiazolines to carbonates and diazopropane (11). For that reason we prepared unsymmetric bis-benzyloxy oxadiazolines in order to have internal competition in a carbene that could fragment to either the benzyl radical and a *p*-substituted benzyloxycarbonyl radical or to a *p*-substituted benzyl radical and the benzyloxycarbonyl radical. We now report the results of that study.

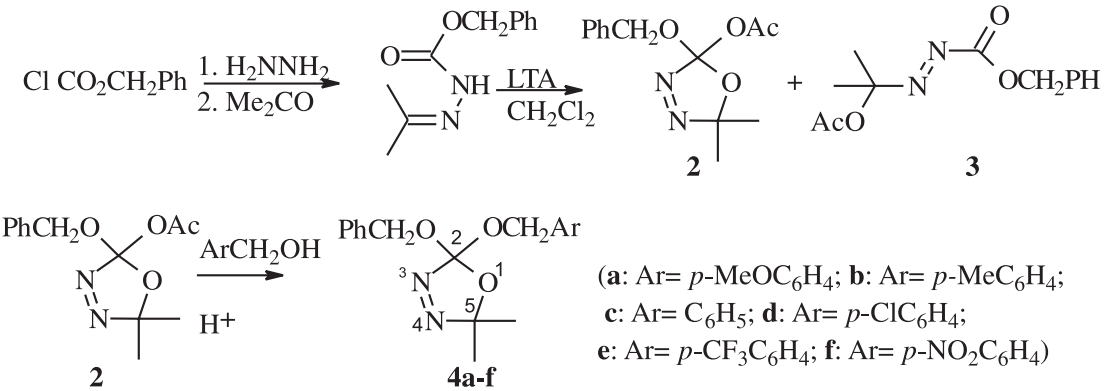
Methods results and discussion

The oxadiazoline substrates (**4a**–**f**) were prepared from a common precursor, namely 2-acetoxy-2-benzyloxy oxadiazoline (**2**), by means of the substitution reaction in Scheme 3. Precursor **2** was obtained by oxidative cyclization of the benzyloxycarbonyl hydrazone of acetone with lead tetraacetate in dichloromethane, which afforded **2** and **3** in the ratio 60:40. Although that mixture could be used directly for the substitution, substantial purification was achieved by washing with base and subsequent chromatography on silica. The oxadiazoline produced in this way did contain a small amount (ca. 5%) of dibenzyl carbonate and the final yield of that product from the thermolysis was corrected for the

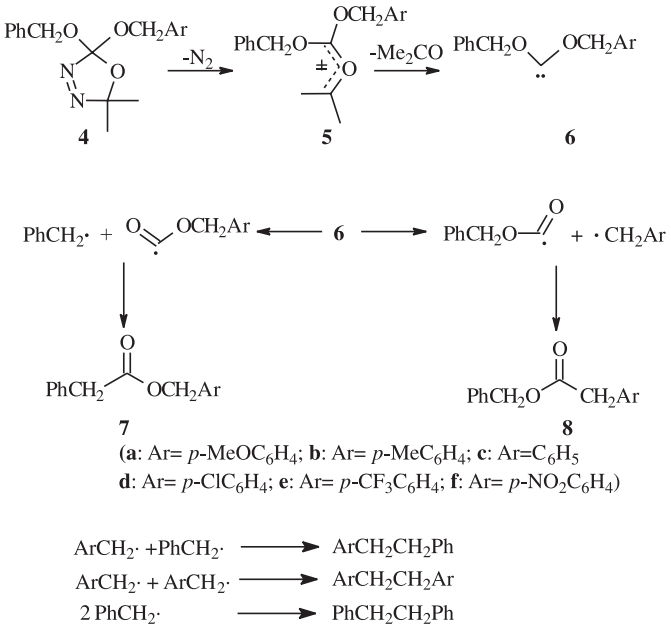
Scheme 2.



Scheme 3.



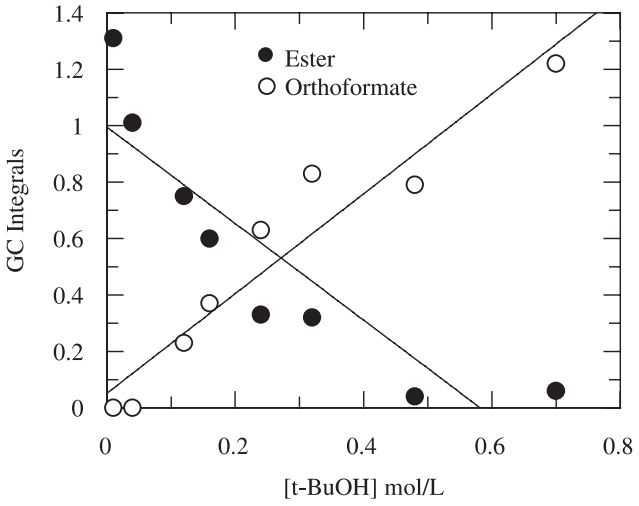
Scheme 4.



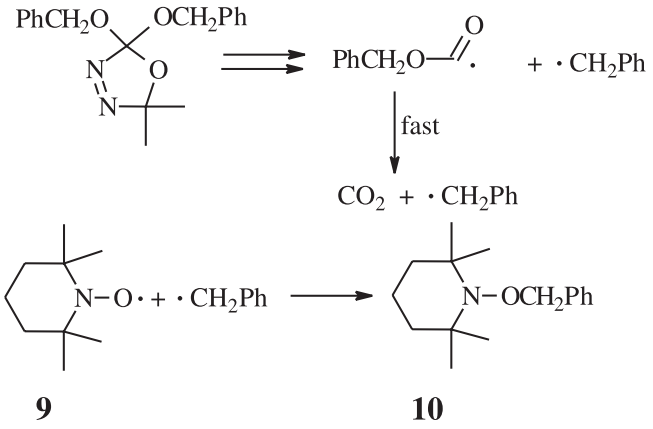
quantity initially present. Thermolyses were done in evacuated, sealed glass tubes that were heated for 24 h at 110.0 ± 0.1°C with an oil bath.

The mechanism of thermolysis of oxadiazolines analogous to **4** generally involves 1,3-dipolar cycloreversion in the first step, to afford a carbonyl ylide intermediate (12–14). The latter then fragments to acetone and a dialkoxycarbene, Scheme 4. An alternative mechanism, proposed by Smith (15) on the basis of computation, involving concerted fragmentation to N_2, acetone, and dialkoxycarbenes, cannot be ruled out for an oxadiazoline with new substituents. In the present case, knowledge of the mechanism by which the carbene intermediate is generated is not critical, nor does the carbene have to be formed in essentially quantitative yield. In Scheme 4, stepwise fragmentation is illustrated with the important feature being the intramolecular competition in the fragmentation of carbene **6**. Formation of a carbene intermediate was established by trapping **6c** with *tert*-butyl alcohol (Fig. 1). It was assumed that the other oxadiazolines formed analogous carbenes, albeit not necessarily with the same efficiency. Products from thermolysis of **4c** in the absence of a trap included acetone (88%),[2] bibenzyl (14%), benzyl phenylacetate (29%), dibenzyl carbonate (6%), a trace of benzyl alcohol, benzyl formate (22%), and tribenzyl orthoformate (19%). The latter two are presumably derived from adventitious water, which traps the carbene intermediate to form benzyl formate and benzyl alcohol via the hemi orthoformate. Benzyl alcohol then traps the carbene to generate the orthoformate. Products from **4a**, **b**, and **d**–**f** were more complex, containing three bibenzyls (primarily $ArCH_2CH_2Ph$, with smaller amounts of $PhCH_2CH_2Ph$ and $ArCH_2CH_2Ar$), two orthoformates, ($HC(OPh)_2OAr$ and

Fig. 1. GC integrals, on an arbitrary scale, vs. concentration of *tert*-BuOH. The scatter is believed to be caused by the various concentrations of adventitious water.



Scheme 5.

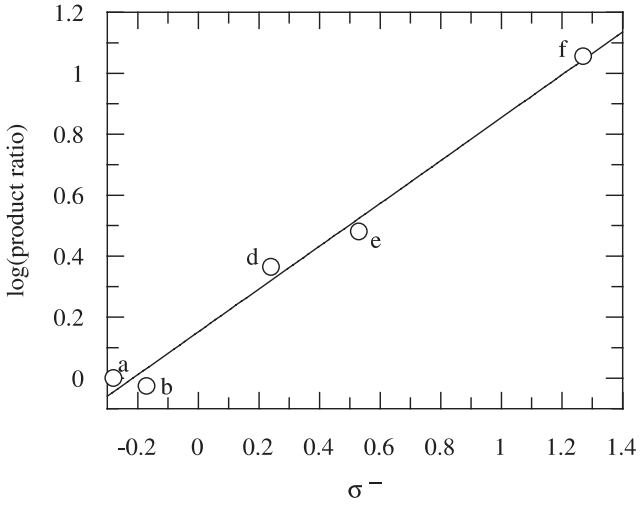


$HCOPh(OAr)_2$), an unsymmetric carbonate ($ArOCO_2Ph$) (all indicated by GC/MS), and two esters. The product composition was not determined in detail but it was possible to determine the relative yields of esters **7** and **8** in each case, although the C_6D_6 had to be evaporated and replaced with CCl_4 in the case of products from **4a** because the ^1H NMR signals of interest were not resolved in benzene solution. Identities of the isomers **7** and **8** in each of the reaction mixtures were secured through comparison with the ^1H NMR spectra of authentic compounds.

The bibenzyls are strong indicators of radical chemistry and radical intermediates were confirmed by capturing benzyl radicals from **4c** with TEMPO, Scheme 5. Trapping of benzyloxycarbonyl radicals with TEMPO was not to be expected because the rate constant for decarboxylation of benzyloxycarbonyl radicals has the value $k_{110°C} \approx 10^9\ s^{-1}$ (extrapolated from published data) (16). In the case of benzyloxymethoxycarbene, both the methoxycarbonyl and benzyl radicals were trapped with TEMPO (**9**) (11).

[2] We have not always used an adequate pulse delay when examining oxygen-free solutions by ^1H NMR spectroscopy. The yield of acetone, in particular, comes out too low if an inadequate pulse delay is used.

Fig. 2. Logarithms of the ratios of esters (**8**/**7**) versus σ^- substituent constants.



The sense and magnitude of the selectivity in the carbene fragmentation step should be reflected in the relative yields of esters **7a**, **b**, **d**–**f** and **8a**, **b**, **d**–**f** from the corresponding precursors (**4a**, **b**, **d**–**f**). The results show clearly that there is selectivity in the sense favouring fragmentation to afford the benzylic radical with an electron-withdrawing group in the *para* position. The ratios (**8**:**7**) were: **a**, 1.0; **b**, 0.94; **d**, 2.3; **e**, 3.0; **f**, 11.4. A good correlation of logarithms of product ratios (assumed to reflect the ratios of fragmentation rate constants well) with σ^- substituent constants was found, with $\rho_{(PhH,\ 110°C)} = 0.7$, (Fig. 2), indicating that the fragmentation of the carbenes is lower in energy if electron density is allowed to increase at the carbon atom that is becoming the benzylic radical fragment. A corollary is that the electron density at the other developing fragment must decrease correspondingly. The correlation with σ^- suggests that the fragmentation has more polar character (benzyl anion-like and benzyloxycarbonyl cation-like) than radical character. Whether or not there is a transition state for the homolysis is not known. For homolysis of a model system there is a transition state only for the conformation with the departing group *syn* to the carben's lone pair (9).

The benzyloxycarbonyl–benzyl radical pair is formed in the singlet state (9, 10, 17) in a solvent cage. Coupling in the cage must be very fast, given that it can compete with both decarboxylation of the benzyloxycarbonyl radical and diffusive separation of that pair. Very fast coupling of such pairs is reasonable, given that the rate constant for cage coupling is not limited by diffusion but only by a very small kinetic barrier, if any. An alternative explanation would have the esters originating from 1,2-rearrangement of the carbenes rather than from radical coupling. Carbene rearrangement is very unlikely, given that computation shows the barrier to fragmentation to be much lower than that for 1,2-rearrangement in allyloxyhydroxycarbene, a model for **6** (17).

Experimental

General

Although some of the compounds encountered in this work have been reported previously, NMR and spectra were generally not included. We report NMR spectra for both $CDCl_3$ and C_6D_6; the latter because reactions were run in C_6D_6. Chemical shifts (ppm) for $CDCl_3$ are referenced to TMS, while those for C_6D_6 are referenced to *p*-xylene (2.10 ppm) or 1,4-dimethoxybenzene (6.80 ppm). The numbers in brackets in the MS data are relative signal intensities.

Synthesis of oxadiazolines (4)

A solution of benzyl chloroformate (10.0 mL, 0.071 mol) in ether (72 mL) was added slowly (ca. 1 h) to a cooled solution (–5°C) of hydrazine monohydrate (16.8 mL, 0.33 mol) in ether (10.0 mL) (18). After addition, the ice bath was removed and stirring was continued for 1 h. The white precipitate formed during the reaction dissolved upon the addition of water. The ether layer was separated and washed three times with water (25 mL) before it was dried with magnesium sulphate. After filtering, the ether was removed with a rotary evaporator to leave benzyl hydrazinocarboxylate as a white solid (7.55 g, 0.045 mol), 82% yield, mp 65–66°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.74 (s, 2H, NH_2), 5.12 (s, 2H, CH_2O), 6.12 (s, 1H, NH), 7.3 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 67.34 (CH_2), 128.21, 128.34, 128.57, 136.03, 155.55 (C=O); MS (EI) *m*/*z*: 122 (9), 91 (100), 65 (9); MS (CI, NH_3) *m*/*z*: 184 ($(M + NH_4)^+$, 33), 167 ($(M + H)^+$, 100), 123 (12), 108 (21), 91 (62).

Magnesium sulphate (5g) was added to a solution of benzyl hydrazinocarboxylate (7.55 g, 0.045 mol) in 40 mL of acetone and the reaction mixture was stirred overnight. The magnesium sulphate was removed by vacuum filtration and the solvent was removed with a rotary evaporator. The resultant white solid (**1**) (7.15 g, 82%) melted at 75–77°C, lit (19) mp 85°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.76 (s, 3H), 2.00 (s, 3H), 5.21 (s, 2H), 7.34 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 16.08 (CH_3), 25.28 (CH_3), 67.33 (CH_2), 128.31, 128.41, 128.52, 135.98, 151.14 (C=N), 154.80 (C=O); MS (EI) *m*/*z*: 206 (M^+, 1), 91 (100), 65 (10), 49 (22); MS (CI, NH_3) *m*/*z*: 207 ($(M + H)^+$, 100), 91 (32).

Acetone benzyloxycarbonyl hydrazone (7.15 g, 0.037 mol) in dichloromethane (70 mL) was added dropwise to a solution of lead (IV) acetate (28.0 g, 0.106 mol) in ice-cold dichloromethane (60 mL) under nitrogen. After the addition the ice bath was removed and the solution was stirred for two hours. The mixture was filtered through Celite and washed once with water and twice with 5% sodium bicarbonate. After filtration through a layer of Celite to remove additional lead salts, the dichloromethane layer was dried over magnesium sulphate. Fitration and evaporation of the solvent left a yellow oil (5.43 g, 58%) which was a mixture of the oxadiazoline **2** (60 parts) and the acyclic by-product **3** (40 parts). ^{1}H NMR of **2** (200 MHz, $CDCl_3$) δ: 1.52 (s, 3H, CCH_3), 1.67 (s, 3H, CCH_3, 2.10 (s, OAc, overlapping with OAc signal from **3**), 4.91 (d, ^2J = 8.6 Hz, 1H), 4.99 (d, ^2J = 8.6 Hz, 1H), 7.2–7.5 (m, overlapping with m from **3**, the overlapping signals integrated satisfactorily; ^{1}H NMR of **3** (200 MHz, $CDCl_3$) δ: 1.63 (s, 6H, $C(CH_3)_2$, 2.10 (s, OAc, overlapping with OAc signal from **2**), 5.40 (s, 2H, CH_2), 7.2–7.5 (m, overlapping with m from **2**), the overlapping signals integrated satisfactorily; ^{13}C NMR (composite spectrum, 50 MHz, $CDCl_3$) δ: 20.51 (H_3CC=O), 21.39 (H_3C-C=O), 22.45 (CH_3), 24.12 (CH_3), 24.47 (CH_3), 25.27 (CH_3), 67.51 (CH_2), 69.96 (CH_2), 122.47 (C5), 127.89, 128.10,

128.45, 128.66, 128.71, 128.79, 133.18, 134.14, 136.08 (C2), 166.45 (O(C=O) 169.17 (N-C=O-O).

Benzyl alcohol (0.48 g, 4.4 mmol) and a mixture of **2** and **3** (above, 0.10 g, 3.7 mmol) were dissolved in dichloromethane (30 mL) before trifluoroacetic acid (0.096 mL, 1.25 mmol) was added to the reaction mixture. After stirring for approximately 1 h, progress was monitored by ^{1}H NMR spectroscopy, revealing that the pair of doublets at 4.93 ppm had been replaced with a new pair of doublets at 4.85 ppm (200 MHz, $CDCl_3$). Aqueous NaOH (35 mL) was added and the mixture was stirred for another hour. The dichloromethane layer was separated, washed twice with water (15 mL), and dried over magnesium sulphate. After filtration and removal of the dichloromethane the components of the reaction mixture were separated by means of centrifugal chromatography (Chromatotron, 100% hexanes). The pale yellow oil obtained (0.29 g, 41%) was **4c** containing about 4.5% of dibenzylcarbonate. ^{1}H NMR (300 MHz, C_6D_6) δ: 1.30 (s, 6H), 4.80 (d, ^2J = –11.6 Hz, 2H, CH_2Ph), 4.91 (d, ^2J = –11.6 Hz, 2H, CH_2Ph), 7.06–7.41 (m, 10H); ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.50 (s, 6H), 4.76 (d, ^2J = –11.4 Hz, 2H, CH_2Ph), 4.86 (d, ^2J = –11.4 Hz, 2H, CH_2Ph), 7.30–7.35 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 24.1 (CH_3), 66.9 (CH_2), 119.6 (C5), 127.8, 127.9, 128.4, 136.2 (C2), 136.7.

Oxadiazolines **4a**, **b**, and **d**–**f** were prepared by the above procedure for **4c**, with substituted benzyl alcohols instead of benzyl alcohol

4a: Yellow oil, yield 53%; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.59 (s, 6H), 3.79 (s, 3H), 4.72 (d, ^2J = –11.2 Hz, 1H), 4.78 (d, ^2J = –11.5 Hz, 1H), 4.83 (d, ^2J = –11.2 Hz, 1H), 4.88 (d, ^2J = –11.5 Hz, 1H), 6.86 (d, ^3J = 8.62 Hz, 2H) 7.29–7.33 (m, 7H); ^{1}H NMR (200 MHz, C_6D_6) δ: 1.23 (s, 3H), 1.25 (s, 3H), 3.27 (s, 3H), 4.72–4.92 (m, 4H), 6.69 (d, ^3J = 6.6 Hz, 2H), 6.71–7.25 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 24.01, 55.14, 66.56, 66.69, 113.71, 119.32 (C5), 127.67, 128.27, 128.67, 129.45, 136.66 (C2, PhC1), 159.31(ArC4) MS (EI) *m*/*z*: 191 (3), 163 (51), 121 (100), 91 (87), 84 (24), 43 (24); MS (CI, NH_3) *m*/*z*: 260 (4), 163 (20), 121 (100), 108 (23), 65 (8), 43 (12).

4b: Clear oil, yield 41%; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.59 (s, 6H), 2.35 (s, 3H), 4.74 (d, ^2J = –11.0 Hz, 1H), 4.83 (d, ^2J = –11.0 Hz, 2H), 4.89 (d, ^2J = –11.4 Hz, 1H), 7.14–7.35 (m, 9H); ^{1}H NMR (300 MHz, C_6D_6) δ: 1.24 (s, 2H), 1.25 (s, 3H), 2.09 (s, 3H), 4.73–4.94 (m, 4H), 6.90–7.28 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.09, 24.04, 66.72, 119.37 (C5), 127.71. 127.84, 128.29, 128.99, 133.56, 136.55 (C2), 136.67; MS (EI) *m*/*z*: 181 (3), 105 (95), 91 (100), 43 (10); MS (CI, NH_3) *m*/*z*: 274 (3), 147 (8), 122 (18), 105 (100), 91 (53).

4d: Pale yellow oil, yield 80%; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 6.56 (s, 6H), 4.74 (d, ^2J = –11.6 Hz, 2H), 4.84 (d, ^2J = –11.6 Hz, 2H), 7.24–7.34 (m, 9H); ^{1}H NMR (300 MHz, C_6D_6) δ: 1.21 (s, 3H), 1.22 (s, 3H), 4.57 (d, ^2J = –11.8 Hz, 1H), 4.66 (d, ^2J = –11.8 Hz, 1H), 4.68 (d, ^2J = –11.6 Hz, 1H), 4.78 (d, ^2J = –11.6 Hz, 1H), 6.88 (d, ^3J = 8.6 Hz, 2H), 7.00–7.12 (m, 5H), 7.21 (d, ^3J = 8.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.00, 24.07, 66.02, 66.78, 119.63 (C5), 127.69, 127.8, 128.36, 128.48, 129.03, 133.61, 135.19, 136.47 (C5); MS (EI) *m*/*z*: 237 (3), 203 (3), 195 (4), 167 (10), 125 (44), 105 (12), 91 (100); MS (CI, NH_3) *m*/*z*: 294 (5), 142 (12), 125 (33), 91 (100).

4e: Clear oil, yield 68%; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.48 (s, 3H), 1.49 (s, 3H), 4.64 (d, ^2J = –11.5 Hz, 1H), 4.71 (d, ^2J = –13.9 Hz, 1H), 4.75 (d, ^2J = –13.9 Hz, 1H), 4.84 (d, ^2J = –11.5 Hz, 1H), 7.15–7.24 (m, 5H), 7.35 (d, ^3J = 8.0 Hz, 2H), 7.50 (d, ^3J = 8.0 Hz, 2H); ^{1}H NMR (300 MHz, C_6D_6) δ:1.26 (s, 6H), 4.60–4.82 (m, 4H), 6.97–7.26 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 24.00, 24.12, 65.96, 66.87, 119.33 (C5), 125.33, 127.61, 127.72, 127.97, 128.40, 136.43 (C2), 136.64; ^{19}F NMR (282 MHz, $CDCl_3$, ref. CCl_3F) δ: –62.80 (s); MS (EI) *m*/*z*: 249 (2), 229 (2), 159 (56), 133 (57), 91 (100); MS (CI, NH_3) *m*/*z*: 328 (2), 176 (9), 159 (18), 108 (42), 91 (100).

4f: Yellow oil, yield 56%; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 1.57 (s, 3H), 1.59 (s, 3H), 4.71 (d, ^2J = –11.4 Hz, 1H), 4.79 (d, ^2J = –11.4 Hz, 1H), 4.88 (d, ^2J = –13.1 Hz, 1H), 4.97 (d, ^2J = –13.1 Hz, 1H), 7.24–7.32 (m, 5H), 7.47 (d, ^3J = 8.6 Hz, 2H), 8.16 (d, ^3J = 8.6 Hz, 2H); ^{1}H NMR (300 MHz, C_6D_6) δ: 1.23 (s, 6H), 4.53–4.72 (m, 4H), 6.82 (d, ^3J = 8.8 Hz, 2H), 7.00–7.21 (m, 5H), 7.74 (d, ^3J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 23.89, 24.11, 65.46, 66.85, 119.96 (C5), 123.48, 127.64, 127.73, 127.96, 128.36, 136.24, 136.48 (C2), 144.19, 147.36; MS (EI) *m*/*z*: 137 (13), 136 (95), 91 (100), 49 (24), 43 (16); MS (CI, NH_3) *m*/*z*: 254 (2), 153 (13), 136 (24), 107 (60), 91 (100), 60 (16).

Typical thermolysis of an oxadiazoline

The following procedure for **4c** was also followed for the others except that *p*-xylene was the reference. Signals from 1,4-dimethoxybenxene interfered in those cases. Neither internal standard reacted to afford any products detectable by GC/MS.

A solution of dibenzyloxy oxadiazoline (**4c**, 15.9 mg, 0.05mmol) containing 4.6% of dibenzyl carbonate and 1,4-dimethoxybenzene (1.0 mg, 0.0072 mmol) as internal standard, in 0.52 mL of benzene-d_6 in an NMR tube was degassed three times (freeze-pump-thaw sequence) before sealing. The NMR tube was then kept for 24 h in an oil bath at 110 ± 0.1°C. Product yields were determined by ^{1}H NMR spectroscopy, with a pulse delay time of 3 min for products from **4c** and 5 min for the other mixtures, to ensure reliable integral ratios for **7** and **8** (average of 5 intergrations). Chemical shifts (CH_2CO) in C_6D_6 (those of **7a** and **8a** in CCl_4) used for measurement of those relative yields were: *p*-xylene, 2.10; 1,4-dimethoxybenzene, 6.80; **7a**, 3.52; **8a**, 3.48; **7b**, 3.32; **8b**, 3.34; **7d**, 3.29; **8d**, 3.12; **7e**, 3.31; **8e**, 3.14; **7f**, 3.31; **8f**, 3.06.

Products from **4c** were: acetone, 88%, ^{1}H NMR (200 MHz, C_6D_6) δ: 1.606 (s). Bibenzyl, 14%, ^{1}H NMR (200 MHz, C_6D_6) δ: 2.78 (s, 4H), 7.02–7.20 (m, overlap with other signals); GC/MS (EI) *m*/*z*: 182 (M^+, 26), 91 (100), 65 (13). Benzyl phenylacetate, 29%, ^{1}H NMR (200 MHz, C_6D_6) δ: 3.38 (s, 2H), 4.96 (s, 2H), 7.02–7.20 (m, overlap with other signals); GC/MS (EI) *m*/*z*: 226 (M^+, 1), 91 (100), 65 (10). Dibenzyl carbonate, 6%, ^{1}H NMR (200 MHz, C_6D_6) δ: 4.98 (s, 4H), 7.02–7.20 (m, overlap with other signals), GC/MS (EI) *m*/*z*: 180 (33), 151 (26), 107 (60), 91 (100), 79 (48), 65 (29). Tribenzyl orthoformate,

19%, ^{1}H NMR (200 MHz, C_6D_6) δ: 4.66 (6H), 5.46 (s, 1H), 7.02–7.20 (overlap with other signals); GC/MS (EI), *m/z*: 197 (9), 181 (10), 107 (10), 91 (100). Benzyl formate, 22%, ^{1}H NMR (200 MHz, C_6D_6) δ: 4.91 (2H), 7.02–7.20 (m, overlap with other signals), 7.60 (1H).

Synthesis of benzyl arylacetate reference compounds

The required arylacetyl chloride **8a**, **b**, **d–f** (0.061 g, 6.4 mmol) was dissolved in benzene (5 mL) and added slowly to a solution of benzyl alcohol (0.16 g, 0.8 mmol) in pyridine (0.2 mL, 2.3 mmol) which was cooled in an ice bath. After addition the stirring was continued for one hour. The benzene layer was washed twice with water (5 mL), and dried with magnesium sulphate. After filtration and evaporation of the benzene, the ^{1}H NMR spectrum in C_6D_6, referenced to *p*-xylene at 2.10 ppm, was recorded.

8c: (20) pale yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.60 (s, 2H), 5.03 (s, 2H), 7.08–7.29 (m, 10H); ^{1}H NMR (300 MHz, C_6D_6) δ: 3.40 (s, 2H), 4.97 (s, 2H), 7.09–7.22 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 41.33, 66.61, 128.18, 128.54, 129.27, 135.83, 171.39 (C=O); ^{13}C NMR (75 MHz, C_6D_6) δ: 41.35, 66.42, 128.2, 128.3, 128.7, 129.6, 134.5, 170.92 (C=O). GC/MS (EI) *m/z*: 226 (M^+, 1), 91 (100), 65 (10).

8a: (21–23) Oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.59 (s, 2H), 3.78 (s, 3H), 5.10 (s, 2H), 6.84 (d, ^3J = 8.6 Hz, 2H), 7.16–7.30 (m, 7H); ^{1}H NMR (300 MHz, C_6D_6) δ: 3.23 (s, 3H), 3.32 (s, 2H), 4.92 (s, 2H), 6.68 (d, ^3J = 8.7 Hz, 2H), 7.00–7.08 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 40.43, 55.26, 66.55, 114.00, 128.10, 128.51, 130.30, 132.29, 172.93 (C=O).

8b: (24) Oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.33 (s, 3H), 3.63 (s, 2H), 5.13 (s, 2H), 7.10–1.33 (m, 9H); ^{1}H NMR (300 MHz, C_6D_6) δ: 2.02 (s, 3H), 3.34 (s, 2H), 4.90 (s, 2H), 6.87–7.12 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 21.03, 40.91, 66.53, 128.09, 128.49, 129.24, 130.83, 135.92, 136.70, 171.57 (C=O); MS (EI) *m/z*: 240 (M^+, 25), 193 (13), 181 (16), 105 (100), 91 (76); MS (CI, NH_3) *m/z*: 258 (($M + NH_4$)$^+$, 13), 241 (($M + H$)$^+$, 5), 216 (79), 108 (51), 91 (100).

8d: (23) oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.60 (s, 2H), 5.10 (s, 2H), 7.16–7.32 (m, 9H); ^{1}H NMR (300 MHz, C_6D_6) δ: 3.13 (s, 2H), 4.88 (s, 2H), 6.76 (d, ^3J = 8.4 Hz, 2H), 6.79–7.15 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 40.52, 66.69, 128.09, 128.24, 128.49, 130.60, 132.25, 133.04, 170.91 (C=O); MS (EI) *m/z*: 260 (M^+, 10), 181 (10), 127 (24), 125 (60), 91 (100), 65 (16), 63 (10); MS (CI, NH_3) *m/z*: 278 (($M + NH_4$)$^+$, 55), 125 (44), 108 (49), 91 (100), 80 (42); HRMS calculated for $C_{15}H_{13}O_2Cl$: 260.0604, found: 260.0603.

8e: Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.71 (s, 2H), 5.13 (s, 2H), 7.28–7.35 (m, 5H) 7.38 (d, ^3J = 8.1 Hz, 2H), 7.56 (d, ^3J = 8.1 Hz, 2H); ^{1}H NMR (300 MHz, C_6D_6) δ: 3.13 (s, 2H), 4.88 (s, 2H), 6.76 (d, ^3J = 8.0 Hz, 2H), 6.79–7.15 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 29.69, 66.95, 125.48, 125.55, 128.24, 128.38, 128.54, 128.61, 129.37, 129.71, 135.61, 137.84, 170.55 (C=O); ^{19}F NMR (282 MHz, $CDCl_3$, ref. CCl_3F) δ: –62.82 (s); MS (EI) *m/z*: 294 (M^+, 3), 181 (8), 159 (5), 108 (21), 91 (100), 65 (10); MS (CI, NH_3) *m/z*: (($M + NH_4$)$^+$, 5), 159 (5), 108 (21), 91 (100); HRMS calculated for $C_{16}H_{13}O_2F_3$: 294.0867, found: 294.0872.

8f: pale yellow solid, mp 80–84°C, lit. (25) mp 90–92°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.76 (s, 2H), 5.14 (s, 2H), 7.29–7.35 (m, 5H), 7.43 (d, ^3J = 8.7 Hz, 2H), 8.16 (d, ^3J = 6.6 Hz, 2H); ^{1}H NMR (300 MHz, C_6D_6) δ: 3.03 (s, 2H), 4.27 (s, 2H), 4.86 (s, 2H), 6.66 (d, ^3J = 8.7 Hz, 2H), 6.93–7.07 (m, 5H), 7.69 (d, ^3J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 40.96, 67.14, 123.73, 126.97, 128.61, 130.29, 135.35, 141.12, 169.98; MS (EI) *m/z*: 271 (M^+, 8), 136 (8), 91 (100), 65 (9); MS (CI, NH_3) *m/z*: 289 (($M + NH_4$)$^+$, 6), 271 (M^+, 3), 135 (10), 108 (9), 91 (100); HRMS calculated for $C_{15}H_{13}NO_4$: 271.0845; found: 271.0827.

Synthesis of 4-substituted-benzyl phenylacetates (7a–f)

A solution of phenylacetyl chloride (0.51 g, 3.0 mmol) in benzene (5 mL) was added slowly to a cooled solution of the appropriate arylmethanol (0.4 g, 3.0 mmol) in pyridine (0.5 mL, 9.0 mmol). After one hour the benzene solution was washed twice with water and dried with magnesium sulphate. Benzene was removed with a rotary evaporator. Some of the esters were purified by radial chromatography (Chromatotron, 10% EtOAc in hexanes).

7a: (21,22) Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.61 (s, 2H), 3.77 (s, 2H), 5.04 (s, 2H), 6.83–6.87 (m, 2H), 7.20–7.28 (m, 7H); ^{1}H NMR (300 MHz, C_6D_6) δ: 3.20 (s, 3H), 3.32 (s, 2H), 4.89 (s, 2H), 6.65 (d, ^3J = 8.7 Hz, 2H), 7.00–7.10 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 41.28, 55.17, 66.37, 113.56 (C2), 126.97, 127.93, 128.46, 129.19, 129.89, 133.90, 159.55, 171.39 (C=O); MS (EI) *m/z*: 256 (M^+, 21), 121 (100), 91 (37); MS (CI, NH_3) *m/z*: 256 (M^+, 8), 138 (8), 121 (100).

7b: (24) Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.34 (s, 3H), 6.65 (s, 2H), 5.08 (s, 2H), 7.13–7.31 (m, 9H); ^{1}H NMR (300 MHz, C_6D_6) δ: 2.00 (s, 3H), 3.32 (s, 2H), 4.91 (s, 2H) 6.85–7.12 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 21.16, 41.36, 66.57, 127.06, 128.27, 128.55, 129.21, 129.27, 132.89, 133.95, 138.03, 171.41(C=O); MS (EI) *m/z*: 240 (M^+, 16), 209 (5), 105 (100), 91 (46), 65 (12); MS (CI, NH_3) *m/z*: (($M + NH_4$)$^+$, 26), 154 (16), 105 (100), 91 (34), 65 (5).

7d: Oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.63(s, 2H), 5.05 (s, 2H), 7.17–7.29 (m, 9H); ^{1}H NMR (300 MHz, C_6D_6) δ: 3.29 (s, 2H), 4.69 (s, 2H), 6.73 (d, ^3J = 8.4 Hz, 2H), 6.93–7.12 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 41.23, 65.64, 127.10, 128.52, 128.62, 129.17, 133.67, 134.29 (C2), 171.19 (C=O); MS (EI) *m/z*: 260 (M^+, 8), 125 (87), 91 (100), 65 (18), 51 (5); MS (CI, NH_3) *m/z*: 278 (($M + NH_4$)$^+$, 55), 260 (M^+, 5), 184 (42), 125 (100), 108 (19), 91 (39); HRMS calculated for $C_{15}H_{13}O_2Cl$: 260.0604 found: 260.0603.

7e: Yellow solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.66 (s, 2H), 5.14 (s, 2H), 7.22–7.29 (m, 5H), 7.35 (d, ^3J = 8.0 Hz, 2H), 7.55 (d, ^3J = 8.1 Hz, 2H); ^{1}H NMR (300 MHz, C_6D_6) δ: 3.31 (s, 2H), 4.69 (s, 2H), 6.80 (d, ^3J = 8.0 Hz, 2H), 7.00–7.12 (m, 5H), 7.20 (d, ^3J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 4.21, 65.45, 125.40, 127.17, 127.87, 128.53, 129.17, 133.53 (C2), 139.76, 171.06 (C=O); ^{19}F NMR

(282 MHz, $CDCl_3$) δ: –62.89 (s); MS (EI) *m/z*: 294 (M^+, 8), 159 (60), 109 (18), 91 (100), 65 (33), 49 (82); MS (CI, NH_3) *m/z*: 312 ($(M + NH_4)^+$, 90), 272 (8), 176 (16), 159 (18), 108 (71), 91 (100); HRMS calculated for $C_{16}H_{13}O_2F_3$: 294.0868, found: 294.0858.

7f: White solid mp 59–61°C; ^1H NMR (300 MHz, $CDCl_3$) δ: 3.67 (s, 2H), 5.18 (s, 2H), 7.22–7.32 (m, 5H), 7.37 (d, ^3J = 8.6 Hz, 2H), 8.13 (d, ^3J = 8.1 Hz, 2H); ^1H NMR (300 MHz, C_6D_6) δ: 3.31 (s, 2H), 4.60 (s, 2H), 6.63 (d, ^3J = 8.7 Hz, 2H), 7.01–7.12 (m, 5H), 7.68 (d, ^3J = 8.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 41.18, 64.90, 123.65, 127.26, 128.06, 129.16, 133.38, 143.03, 147.59, 170.93 (C=O); MS (EI) *m/z*: 271 (M^+, 5), 136 (5), 106 (3), 91 (100), 65 (10); MS (CI, NH_3) *m/z*: 289 ($(M + NH_4)^+$, 8), 271 (M^+, 2) 135 (11), 108 (10), 91 (100), 65 (6). HRMS calculated for $C_{15}H_{13}NO_4$: 271.0845, found: 271.0861.

Dibenzylcarbonate

To benzyl alcohol (1.5 g, 13 mmol) and pyridine (0.98 g, 12.3 mmol) in 60 mL of dichloromethane under nitrogen, 1,1-carbonyldiimidazole (1 g, 6.1 mmol) in 20 mL of dichloromethane was added during 1 h. The solution was stirred overnight, washed once with water, twice with 5% HCl, once with water, and then with brine. Drying with magnesium sulphate, filtration, and removal of the solvent left crude dibenzyl carbonate that was purified by centrifugal chromatography, mp 28–29°C (lit. (26) mp 27.3–29.1°C); ^1H NMR (200 MHz $CDCl_3$) δ: 5.09 (s, 4H), 7.13–7.37 (m, 10H); ^1H NMR (200 MHz, C_6D_6) δ: 4.94 (s, 4H), 7.04–7.17 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 69.58 (CH_2), 128.21, 128.47, 135.13, 154.99 (C=O); MS (EI) *m/z*: 180 (4), 151 (5), 107 (32), 91 (100), 79 (32), 65 (14), 51 (11); MS (CI) *m/z*: 260 ($(M + NH_4)^+$, 100), 243 $(M + H)^+$, 10), 198 (26), 181 (32), 108 (73), 91 (72).

Tribenzylorthoformate

To **4c** (30.3 mg, 0.106 mmol, containing 9% carbonate) in benzene (1 mL) was added dimethoxybenzene (3.6 mg, 0.026 mmol, internal standard) and benzyl alcohol (60.6 mg, 0.56 mmol). The solution was flame sealed into an NMR tube after three freeze-pump-thaw cycles and heated at 110°C for 24 h. Column chromatography with 10% EtOAc in hexanes yielded tribenzylorthoformate (27). ^1H NMR (200 MHz, $CDCl_3$) δ: 4.66 (s, 6H), 5.43 (s, 1H), 7.24–7.35 (m, 15H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 66.33, 111.51 (orthoformyl), 127.71, 127.88, 128.41, 128.58, 137.46.

Benzyl formate

Benzyl alcohol (2.16 g, 0.02 mol), ethyl formate (1 g, 0.013 mol) and a catalytic amount of H_2SO_4 were dissolved in 10 mL of benzene and heated at 50°C for 24 h. After cooling the solution was washed with 10 mL of 10% NaOH and then with 10 mL of saturated NaCl. Evaporation of the solvent and unreacted ethyl formate left benzyl formate (28) that was purified by means of centrifugal chromatography (Chromatotron, 10% EtOAc in hexanes). ^1H NMR (200 MHz, $CDCl_3$) δ: 4.60 (s, 2H), 7.23–7.43 (m, 5H), 8.13 (s, 1H); ^1H NMR (200 MHz, C_6D_6) δ: 4.91 (s, 2H), 7.12–7.15 (m. 5H), 7.63 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ: 65.64, 128.32, 128.48, 128.62, 135.19, 160.71 (C=O).

Ratios of non-ester products

The thermolysis mixtures from the substituted dibenzyloxy oxadiazolines **4a**, **b**, **d**, and **e** were analyzed by means of GC/MS (DB-5 capillary column, i.d. 0.25 mm) and GC/FID (DB-1 megabore column, 0.53 mm i.d., flow rate 15 mL/min) equipped with an integrator. Both separated all of the products except the isomeric esters. Correction factors were used to correct the responses from the FID (29). Thermolysis of each of the substrates **4a**, **b**, and **d**–**f** gave 2 benzyl formates and 3 bibenzyls, which were identified from their mass spectra, as well as two orthoformates. Ratios were estimated from GC/FID data. Identification of benzyl formate, bibenzyl and tribenzyl orthoformate was confirmed by comparison with the GC trace of authentic samples.

The following are some product ratios. Benzyl formates, HCO_2CH_2Ph:HCO_2CH_2Ar from **4a**, 1.0:0.79; **4b**, 1.0:0.42; **4d**, 1.0:1.5; **4e**, 1.0:1.6. Bibenzyls, $PhCH_2CH_2Ph$:$PhCH_2CH_2Ar$:$ArCH_2CH_2Ar$ from **4a**, 1.0:1.7:0.40; **4b**, 1.0:1.8:0.85; **4d**, 1.0:1.7:0.70; **4e**, 1.0:1.9:0.74. Orthoformates, $HC(OCH_2Ph)_2OCH_2Ar$:$HCOCH_2Ph(OCH_2Ar)_2$ from **4a**, 0.39:1.0; **4b**, 1.15:1.0; **4d**, 1.06:1.0

Thermolysis of 4c in the presence of *tert*-butyl alcohol

A solution of **4c** (224 mg, 0.72 mmol), containing 4.6% dibenzyl carbonate, *tert*-butyl alcohol (1.69 g, 22.9 mmol) and 1,4 dimethoxybenzene (10.1 mg, internal standard) in dry benzene (28 mL) was sealed into a resealable thermolysis tube after three cycles of freeze-pump-thaw degassing. The sealed tube was kept at 110 ± 0.1°C in an oil bath for 24 h. Removal of the solvent and unreacted *tert*-butyl alcohol with a rotary evaporator left dibenzyl *tert*-butyl orthoformate in 43% yield. ^1H NMR (200 MHz, C_6D_6) δ: 1.19 (s, 9H), 4.74 (s, 4H), 5.62 (s, 1H), 7.13–7.43 (m, 10H); ^{13}C NMR (50 MHz, C_6D_6) δ: 28.8 (CH_3), 65.1 (CH_2), 74.2 (CMe_3), 108.8 (orthoformyl), 127.5, 127.9, 128.5, 138.9. Dibenzyl carbonate (3%) was also formed; spectra above.

Thermolysis of 4c in the presence of TEMPO (9)

A solution of **4c** (30.6 mg, 0.098 mmol), **9** (131.4 mg, 0.84 mmol), and 1,4-dimethoxy benzene (2.3 mg, internal standard) in 0.8 mL of dry benzene was degassed as described above before it was sealed into a thermolysis tube for 24 h of heating at 110°C. The products from the thermolysis, listed below, were identified by means of GC/FID (DB-1 column, 30m × 0.53 mm, flow rate 15 mL min^{-1}), by coinjection of authentic samples. A correction factor was applied to the GC integrals for the yield calculations (29).

Benzyl formate, 18%, retention time 10.0 min; **10**, 18%, retention time 26.6 min; benzyl phenylacetate, 13%, retention time 28.1 min; dibenzyl carbonate, 18%, retention time 30.4 min; tribenzylorthoformate, 42%, retention time 41.2 min.

Synthesis of authentic 10

Adduct **10** was prepared from TEMPO, toluene, and di-*tert*-butylperoxide as described previously (11).

Thermolysis rate constant for 4c

The rate of fragmentation of **4c** was monitored by ^1H NMR spectroscopy (200 MHz). A solution of **4c** (16.9 mg, 0.05 mmol) and *p*-xylene (1 μL, 0.008 mmol) in benzene-d_6 (0.54 mL) was sealed into an NMR tube after three sequences

of freeze-pump-thaw degassing. The tube was removed at intervals from an oil bath at 110°C and cooled to room temperature before the ^{1}H NMR spectrum was obtained. Corrections to the time scale were not made for cooling and reheating of the contents of the tube.

A plot of ln (I_t/I_0) vs. time, where I_t and I_0 are the normalized integrals for the oxadiazoline CH_3 hydrogens at time t and time zero, was linear (12 data points, r = 0.9963). The first order decomposition rate constant ($k_{110°C} = 8.7 \times 10^{-5}$ s^{-1}) was obtained from the slope of the least squares line through the origin. The fragmentation of **4f**, followed by the above procedure, gave $k_{110°C} = 7.9 \times 10^{-5}$ s^{-1} (r = 0.9985).

Dependence of product yields on concentration of *tert*-BuOH

Solutions of dibenzyloxy oxadiazoline (**4c**, 0.023 M), 1,4-dimethoxybenzene (0.009 M) and *tert*-BuOH (0.01, 0.04, 0.08, 0.12, 0.16, 0.24, 0.32, 0.18, and 0.70 M) in one mL of benzene were heated at 110°C for 24 h after being flame sealed into an NMR tube following degassing by means of the freeze-pump-thaw cycle. Plots of the normalized GC integrals, for the ester and for dibenzyl *tert*-butyl orthoformate, against the *tert*-BuOH concentration, are in Fig. 1.

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