Synthesis of 1,2,4-dioxazolidine derivatives by the ozonolysis of indenes in the presence of primary amines

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Ozonolysis of indenes in the presence of primary amines gives in each case the corresponding 1,2,4-dioxazolidines derived from the intramolecular cyclization of the products of trapping of the carbonyl oxide moieties by the amines.

Carbonyl oxides, the key intermediate in ozonolysis, are well known to be efficiently captured by alcoholic solvents to yield the corresponding α-alkoxyalkyl hydroperoxides.[1] Similar trapping by amines is less well known. Schulz *et al.*[2a] have found that treatment of a mixture of hex-1-ene and cyclohexylamine with ozone leads to the formation of the corresponding α-aminoalkyl hydroperoxide, albeit in a low yield (20%). Amonozolysis of indene in aqueous ammonia gives isoquinoline (61%), which may be derived from cyclocondensation of the corresponding dialdehyde and ammonia.[3] These results raise the question as to whether the trapping of the carbonyl oxide by an amine is an inefficient process or if the solvent-captured ozonolysis products are too labile to be isolated in reasonable yield.[4] To answer this question, we have ozonolysed indene derivatives in the presence of primary amines in diethyl ether and have obtained in high yields novel bicyclic peroxides having a 1,2,4-dioxazolidine structure,[5,6] derived from the intramolecular cyclization of the carbonyl oxide-captured intermediates.

Results and discussion

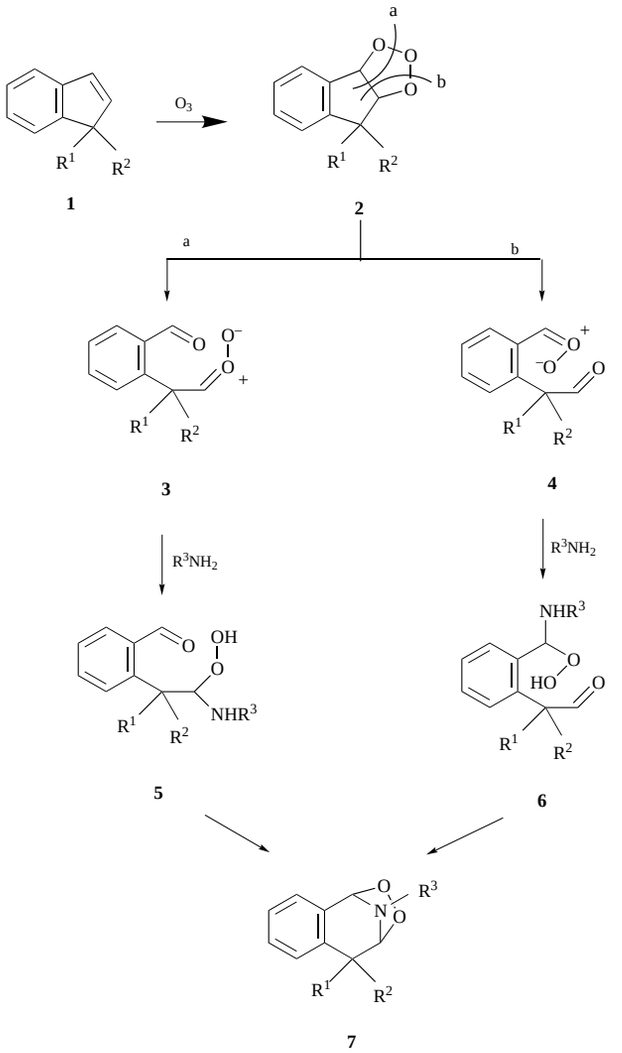
Treatment of a mixture of the indene **1d** (2 mmol) and *tert*-butylamine **4a** (10 mmol) with ozone (1.5 equiv.) in diethyl ether at −70 °C, followed by column chromatography on silica gel, gave the 1,2,4-dioxazolidine derivative **7da** (89%; Scheme 1). Similarly, the corresponding 1,2,4-dioxazolidines **7ca**,**ea** were obtained from the indenes **4c**,**e** in excellent yields. In the case of the indene **1a**, the ^{1}H NMR spectrum of the crude reaction mixture suggested that the dioxazolidine **7aa** had been produced almost quantitatively. However, the cyclic peroxide was labile on silica gel, thereby making isolation of the pure dioxazolidine **7aa** quite difficult. The peroxide **7aa** was isolated by column chromatography on alumina albeit in a low yield (15%; Scheme 1). A similar trend was observed for the dioxazolidine **7ba** derived from ozonolysis of 1-*tert*-butylindene **1b** in the presence of *tert*-butylamine. The ^{13}C NMR spectrum of the crude product suggested that the dioxazolidine **7ba** had been produced as a 3:1 mixture of two stereoisomers. Rapid column chromatography on alumina gave the 3:1 mixture of **7ba** (7%). By the subsequent recrystallization from ethyl acetate–hexane, the minor isomer was isolated in a pure state. This leads us to deduce that the presence of the *gem*-dialkyl substituents increases significantly the stability of the dioxazolidine derivative **7**.

Ozonolysis of the indene **1a** in methanol has been found to give a 1:1 mixture of two regioisomeric hemiperacetals,[7] demonstrating that both of the possible carbonyl oxide intermediates, **3a** and **4a**, are present in a 1:1 ratio. Quantitative formation of the 1,2,4-dioxazolidine **7aa** from the ozonolysis of indene **1a** in the presence of *tert*-butylamine, therefore, suggests that (i) ozone reacts with indene **1a** significantly faster than with the primary amine, (ii) the direct capture of both of the carbonyl oxide intermediates, **3a** and **4a**, by the amine occurs highly efficiently yielding the α-aminoalkyl hydroperoxides, **5aa** and **6aa** and (iii) the adducts, **5aa** and **6aa**, undergo an immediate intramolecular cyclization to give the relatively more stable dioxazolidine **7aa**, in excellent yield (Scheme 1).

A variety of primary amines could be used as the trapping agent. Thus, ozonolysis of the indene **1d** in the presence of cyclohexylamine **4b**, benzylamine **4c** and aniline **4d** led to the formation of the corresponding 1,2,4-dioxazolidines, **7db**, **7dc** and **7dd**, respectively (Scheme 1). In contrast, ozonolysis of the indene **1d** in the presence of a secondary amine such as diethylamine, diisopropylamine or pyrrolidine failed to yield the corresponding trapping product. Instead, the unchanged indene **1d** was recovered quantitatively, suggesting that the reaction of ozone and the secondary amine having a relatively lower ionization potential is very fast.[8]

Ozonolysis of pyrene **8** in the presence of *tert*-butylamine (5 equiv.) also gave the expected 1,2,4-dioxazolidine **9a** albeit in a low yield (12%) together with the unchanged pyrene (80%) [eqn. (1)]. This implies that although the corresponding carbonyl oxide intermediate, if formed, could be efficiently captured by the amine, the reactivity of the amine with ozone is similar to that of pyrene, thereby suppressing the effective ozonolysis of pyrene. A similar trend was observed for the ozonolysis in the presence of cyclohexylamine [eqn. (1)].

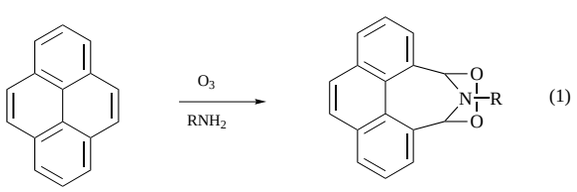
The carbonyl oxide intermediate **11**, derived from ozonolysis of acenaphthylene **10**, was also captured by a primary amine. However, the product was not the expected 1,2,4-dioxazolidine. Instead, the amino-substituted lactone **16** (25%) or the lactam **17** (51%) was obtained, depending on the identity of the primary amines (Scheme 2). This is apparently consistent with the fact that ozonolysis of acenaphthylene in methylene dichloride fails to give the corresponding ozonide, producing, instead, unidentified oligomeric materials. Probably, the formation of highly-strained bicyclic peroxides with either a 1,2,4-dioxazolidine or a 1,2,4-trioxolane structure, is disfavoured and, as a result, alternative modes of decay of the carbonyl oxide intermediate **11** predominate. A plausible mechanism for the formation of the lactone **16** and of the lactam **17** is illustrated in Scheme 2. The structures of the products suggests that dehydration from the rather unstable intermediates **14** or **15** would be very fast.



	R^1	R^2	R^3	**7** (% yield)[a]
7aa	H	H	Bu^t	15 (90)
7ba	Bu^t	H	Bu^t	20 (90)
7ca	Me	Me	Bu^t	75 (80)
7cb	Me	Me	Cyclohexyl	43 (70)
7da	–$(CH_2)_4$–		Bu^t	89 (90)
7db	–$(CH_2)_4$–		Cyclohexyl	78 (90)
7dc	–$(CH_2)_4$–		$PhCH_2$	78 (90)
7dd	–$(CH_2)_4$–		Ph	78 (80)
7ea	–$(CH_2)_2$–		Bu^t	83 (90)

[a] The number in brackets shows the yield of the dioxazolidine **7** determined from the ^{1}H NMR spectrum of the crude reaction mixture.

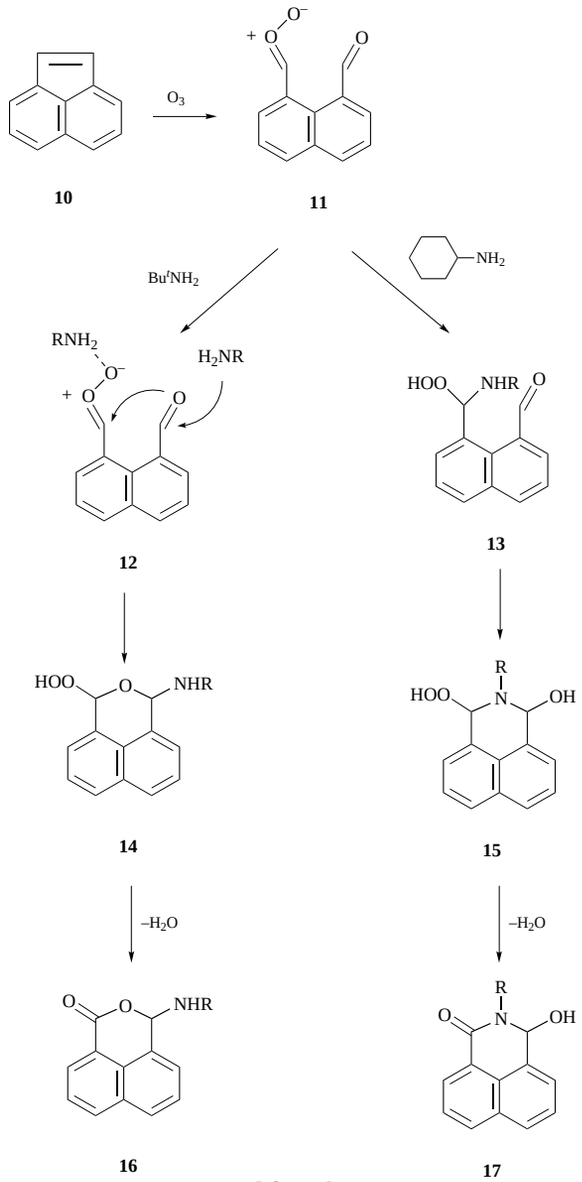
Scheme 1



8

9a R = Bu^t (12%)
9b R = cyclohexyl (12%)

The following results also demonstrate the importance of the substrate structure for the efficient capture of the carbonyl oxide intermediate by the primary amine. Ozonolysis of 2-methylindene and 2-phenylindene in the presence of *tert*-butylamine resulted in exclusive formation of the corresponding ozonides;[9] no evidence was observed for capture of the carbonyl oxide intermediate by the amine. From the ozonolysis



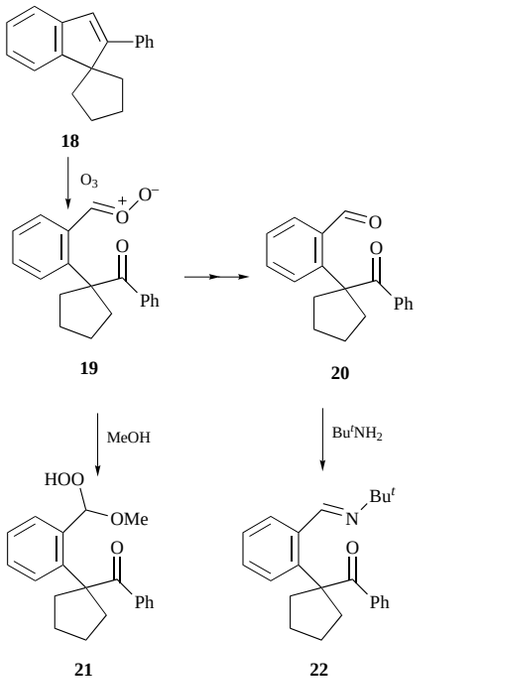
Scheme 2

of 1-phenylcyclopentene under the similar conditions, was obtained the corresponding keto aldehyde, 3-benzoylbutyraldehyde, almost quantitatively. Ozonolysis of 2′-phenylspiro[cyclopentane-1,1′-indene] **18** in the presence of *tert*-butylamine gave the corresponding keto imine **22**. In this respect, the ozonolysis of the indene **18** in methanol has been found to give the α-methoxyalkyl hydroperoxide **21** (as a mixture of the corresponding hemiperacetal) in 96% yield,[10] suggesting that only the carbonyl oxide intermediate **19** participates (Scheme 3). Since the aldehyde oxide moiety in the intermediate **4a** is efficiently captured by *tert*-butylamine, it seems likely that capture of the aldehyde oxide moiety in the intermediate **19** also occurs very easily to give the corresponding *tert*-butylamine-trapped adduct. Exclusive formation of the imine **19**, however, suggests that the intramolecular cyclization of the adduct is slow. Instead, the adduct decomposes into the corresponding keto aldehyde **20** which, in turn, reacts with the amine. In contrast, the reaction of the dialdehyde **23** with *tert*-butylamine gave the aldehyde imine **24**. Subsequent addition of 30% aqueous H_2O_2 resulted in formation of the dioxazolidine **7ea** (43%) [eqn. (2)].

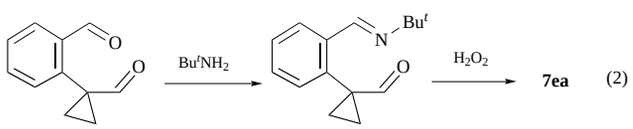
Experimental

General

^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ (unless



Scheme 3



(2)

otherwise noted) with $SiMe_4$ as standard. The method of ozonolysis has previously been described.[11] The indenes **1b–e**[7] and **18**[12] were prepared by the reported method.

CAUTION Since organic peroxides are potentially hazardous compounds, they must be handled with due care; avoid exposure to strong heat or light, mechanical shock, oxidizable organic materials, or transition metal ions. No particular difficulties were experienced in handling any of the new organic ozonides or peroxides synthesized in this work using the reaction scales and procedures described below together with the safeguard mentioned above.

Ozonolysis of the indenes 1a–e in diethyl ether in the presence of primary amines

The ozonolysis of spiro[cyclopentane-1,1′-indene] **1d** in the presence of *tert*-butylamine is representative. A slow stream of ozone (1.5 equiv.) was passed through a solution of the indene **1d** (340 mg, 2 mmol) and *tert*-butylamine (731 mg, 10 mmol) in diethyl ether (20 cm^3) at −70 °C. After evaporation of the mixture, the crude products were separated by column chromatography on silica gel (column, 2 × 50 cm; 20 g of silica gel). Elution with benzene gave the dioxazolidine **7da** (484 mg, 89%). In the case of the dioxazolidines, **7aa** and **7ba**, alumina was used instead of silica gel.

***N-tert*-Butyl-1,3-epidioxy-1,2,3,4-tetrahydroisoquinoline 7aa.** Mp 88–89 °C (Found: C, 71.2; H, 7.9; N, 6.4. $C_{13}H_{17}NO_2$ requires C, 71.2; H, 7.8; N, 6.4%); δ_H 1.20 (9 H, s), 2.97 (2 H, d, *J* 2), 5.53 (1 H, t, *J* 2), 5.83 (1 H, s) and 6.8–7.4 (4 H, m); δ_C 29.74, 38.10, 54.43, 89.51, 90.09, 124.63, 125.89, 128.53, 128.77, 131.98 and 139.96.

Dioxazolidine 7ba. Minor isomer, mp 109–110 °C (from ethyl acetate–hexane) (Found: C, 74.1; H, 9.25; N, 4.9. $C_{17}H_{25}NO_2$ requires C, 74.1; H, 9.15; N, 5.1%); δ_H 1.18 (9 H, s), 1.24 (9 H, s), 3.02 (1 H, d, *J* 2), 5.76 (1 H, d, *J* 2), 5.89 (1 H, s) and 7.0–7.4 (4 H, m); δ_C 28.68, 30.48, 34.47, 54.29, 55.82, 91.11, 91.88, 124.91, 125.79, 128.21, 128.90, 135.60 and 138.63.

Dioxazolidine 7ba. Major isomer, in admixture with 25% of the minor isomer, an oil, δ_H 1.09 (9 H, s), 1.31 (9 H, s), 2.86 (1 H, d, *J* 2.6), 5.82 (1 H, d, *J* 2.6), 5.91 (1 H, s) and 7.0–7.4 (4 H, m); δ_C 29.27, 30.46, 34.45, 55.06, 92.06, 93.21, 124.67, 126.38, 127.75, 130.42, 134.27 and 136.60.

Dioxazolidine 7ca. Mp 104–105 °C (from ethyl acetate–hexane) (Found: C, 72.8; H, 8.7; N, 5.6. $C_{15}H_{21}NO_2$ requires C, 72.8; H, 8.6; N, 5.7%); δ_H 1.33 (12 H, s), 1.35 (3 H, s), 4.93 (1 H, s), 5.77 (1 H, s) and 6.9–7.5 (4 H, m); δ_C 24.85, 28.12, 28.65, 42.63, 53.82, 90.75, 97.77, 124.44, 125.88, 126.51, 129.00, 135.35 and 141.71.

Dioxazolidine 7cb. Oil (Found: C, 74.9; H, 8.5; N, 4.9. $C_{17}H_{23}NO_2$ requires C, 74.7; H, 8.5; N, 5.1%); δ_H 1.0–3.0 (11 H, m), 1.20 (3 H, s), 1.30 (3 H, s), 4.83 (1 H, s), 5.67 (1 H, s) and 6.9–7.5 (4 H, m); δ_C 24.63, 24.92, 25.71, 28.06, 31.13, 32.01, 42.15, 57.13, 91.38, 99.32, 124.96, 125.91, 126.30, 129.18, 134.44 and 141.70; ν_{max}/cm^{-1} 3000, 1570, 1480, 1400, 1120, 890 and 770.

Dioxazolidine 7da. Mp 69–72 °C (from ethyl acetate–hexane) (Found: C, 74.9; H, 8.5; N, 5.1. $C_{17}H_{23}NO_2$ requires C, 74.7; H, 8.5; N, 5.1%); δ_H 1.23 (9 H, s), 1.5–2.5 (8 H, m), 5.00 (1 H, s), 5.77 (1 H, s) and 7.0–7.5 (4 H, m); δ_C 25.79, 25.95, 28.73, 36.75, 40.25, 53.97, 54.51, 90.96, 95.34, 124.30, 125.69, 126.84, 129.31, 135.75 and 142.78; ν_{max}/cm^{-1} 2950, 1370, 1200, 1060, 840 and 750.

Dioxazolidine 7db. Mp 90 °C (from methanol) (Found: C, 75.9; H, 8.5; N, 4.6. $C_{19}H_{25}NO_2$ requires C, 76.2; H, 8.4; N, 4.7%); δ_H 1.0–3.0 (19 H, m), 5.07 (1 H, s), 5.87 (1 H, s) and 6.9–7.5 (4 H, m); δ_C 24.66, 24.70, 25.68, 25.86, 26.02, 31.00, 32.13, 36.91, 40.36, 53.75, 57.22, 91.29, 96.98, 124.78, 125.64, 126.54, 129.42, 134.68 and 142.79.

Dioxazolidine 7dc. Mp 115–116 °C (from ethyl acetate–hexane) (Found: C, 78.1; H, 6.9; N, 4.5. $C_{20}H_{21}NO_2$ requires C, 78.1; H, 6.9; N, 4.6%); δ_H 1.2–2.3 (8 H, m), 4.00 (2 H, s), 4.73 (1 H, s), 5.53 (1 H, s) and 6.8–7.8 (9 H, m); δ_C 25.73, 25.97, 36.90, 40.43, 53.91, 56.67, 94.55, 99.45, 124.99, 125.81, 126.64, 127.68, 128.28, 128.50, 129.19, 129.45, 129.72, 134.16, 137.18 and 142.69; ν_{max}/cm^{-1} 2950, 1370, 1200, 1060, 840 and 750.

Dioxazolidine 7dd. Mp 123–127 °C (from ethyl acetate–hexane) (Found: 77.8; H, 6.45; N, 4.8. $C_{19}H_{21}NO_2$ requires C, 77.8; H, 6.5; N, 4.8%); δ_H 1.5–2.5 (8 H, m), 5.33 (1 H, s), 6.03 (1 H, s) and 7.0–7.5 (9 H, m); δ_C 26.01, 26.24, 37.00, 40.53, 54.41, 93.91, 99.45, 121.81, 124.98, 125.16, 125.96, 126.79, 128.29, 129.36, 129.63, 129.92, 134.17, 142.62 and 147.82.

Dioxazolidine 7ea. Mp 69–72 °C (from ethyl acetate–hexane) (Found: C, 73.5; H, 7.8; N, 5.7. $C_{15}H_{19}NO_2$ requires C, 73.4; H, 6.2; N, 5.7%); δ_H 0.8–1.5 (4 H, m), 1.30 (9 H, s), 4.53 (1 H, s), 5.87 (1 H, s) and 7.0–7.6 (4 H, m); δ_C 13.64, 14.45, 15.95, 28.67, 55.24, 91.24, 97.18, 121.89, 124.59, 125.43, 125.52, 126.52 and 129.18.

Ozonolysis of pyrene 8 in the presence of a primary amine

The reaction in the presence of *tert*-butylamine is representative. A slow stream of ozone (1.5 equiv.) was passed through a solution of pyrene **8** (404 mg, 2 mmol) and *tert*-butylamine (731 mg, 10 mmol) in methylene dichloride (20 cm^3) at −70 °C. After evaporation of the mixture, the products were separated by column chromatography on silica gel. In the first fraction (elution with benzene–hexane, 1:4), pyrene **8** (320 mg, 80%) was eluted. Subsequent elution with benzene gave the dioxazolidine **9a** (81 mg, 12%).

Dioxazolidine 9a. Mp 195–200 °C (from ethyl acetate–hexane) (Found: C, 78.3; H, 6.2; N, 4.5. $C_{20}H_{19}NO_2$ requires C, 78.6; H, 6.3; N, 4.6%); δ_H 1.33 (9 H, s), 6.43 (2 H, s) and 7.7–8.3 (8 H, m); δ_C 28.70, 55.78, 97.31, 126.18, 127.26, 128.30, 130.73, 134.70 and 136.39.

Dioxazolidine 9b. Mp 160–163 °C (from ethyl acetate–hexane) (Found: C, 79.4; H, 6.4; N, 4.2. $C_{22}H_{21}NO_2$ requires C, 79.7; H, 6.4; N, 4.2%); δ_H 0.9–3.0 (11 H, m), 6.13 (2 H, s) and 7.2–8.2 (8 H, m); δ_C 25.41, 25.72, 32.06, 62.16, 99.14, 124.85,

125.77, 126.11, 127.19, 127.30, 128.25, 128.36, 128.86, 130.78, 131.03, 134.59 and 135.92.

Ozonolysis of acenaphthylene in the presence of *tert*-butylamine
A slow stream of ozone (1.5 equiv.) was passed through a solution of acenaphthylene **10** (304 mg, 2 mmol) and *tert*-butylamine (731 mg, 10 mmol) in methylene dichloride (20 cm^3) at −70 °C. After evaporation of the mixture, the products were separated by column chromatography on silica gel. Elution with benzene–diethyl ether (98 : 2) gave the lactone **16** (128 mg, 25%).

3-*tert*-Butylamino-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1-one 16. Mp 130–132 °C (from ethyl acetate–hexane) (Found: C, 75.0; H, 6.7; N, 5.4. $C_{16}H_{17}NO_2$ requires C, 75.3; H, 6.7; N, 5.5%); δ_H 1.36 (9 H, s), 2.30 (1 H, br s), 6.68 (1 H, s), 7.5–7.7 (3 H, m), 7.89 (1 H, d, *J* 4), 8.09 (1 H, d, *J* 4) and 8.43 (1 H, d, *J* 4); δ_C 30.78, 51.14, 89.87, 120.82, 125.34, 126.21, 126.41, 127.91, 128.31, 129.31, 130.97, 132.04, 133.25 and 164.96; ν_{max}/cm^{-1} 3380, 3030, 1710, 1400, 1260, 810 and 740.

Ozonolysis of acenaphthylene in the presence of cyclohexylamine
A slow stream of ozone (1.5 equiv.) was passed through a solution of acenaphthylene **10** (304 mg, 2 mmol) and cyclohexylamine (991 mg, 10 mmol) in methylene chloride (20 cm^3) at −70 °C. After evaporation of the mixture, the products were separated by column chromatography on silica gel. Elution with benzene gave the lactam **17** (286 mg, 51%).

Lactam 17. Mp 185–188 °C (from ethyl acetate–hexane) (Found: C, 76.5; H, 6.8; N, 4.8. $C_{18}H_{19}NO_2$ requires C, 76.8; H, 6.8; N, 5.0%); δ_H 1.2–3.0 (11 H, m), 2.70 (1 H, d, *J* 9), 6.26 (1 H, d, *J* 9) and 7.3–8.4 (6 H, m); ν_{max}/cm^{-1} 3400, 2950, 2800, 1660, 1640, 1600, 1440, 1300, 1010 and 780.

Ozonolysis of 2′-phenylspiro[cyclopentane-1,1′-indene] 18 in the presence of *tert*-butylamine
A slow stream of ozone (1.5 equiv.) was passed through a solution of the indene **18** (492 mg, 2 mmol) and *tert*-butylamine (731 mg, 10 mmol) in methylene dichloride (20 cm^3) at −70 °C. After evaporation of the mixture, the products were separated by column chromatography on alumina. Although the ^{1}H NMR spectrum of the crude mixture of products indicated the formation of only the imine **22**, elution with benzene–diethyl ether (98 : 2) resulted in the isolation of the imine **22** (128 mg, 25%).

Keto imine 22. Oil (Found: C, 82.7; H, 8.2; N, 4.2. $C_{23}H_{27}NO$ requires C, 82.9; H, 8.1; N, 4.2%); δ_H 1.13 (9 H, s), 1.5–2.8 (8 H, m), 6.9–8.1 (9 H, m) and 8.33 (1 H, s); δ_C 25.07, 29.10, 37.82, 57.83, 62.63, 124.79, 127.01, 128.04, 128.14, 128.36, 129.63, 129.92, 131.83, 135.67, 136.11, 143.79, 154.49 and 202.08; ν_{max}/cm^{-1} 2960, 1670, 1450, 1240, 750 and 700.

Synthesis of the dioxazolidine 7ea from the dialdehyde 23
A mixture of the dialdehyde **23** (140 mg, 0.8 mmol) and *tert*-butylamine (292 mg, 4 mmol) in methanol (10 cm^3) was stirred at 20 °C for 1 h. The mixture was then poured into diethyl ether–water and the organic layer was separated and evaporated. The ^{1}H NMR and IR spectra of an aliquot of the crude reaction mixture showed the sole formation of the aldehyde imine **24**: δ_H 7.66 (s) and 8.70 (s); ν_{max}/cm^{-1} 1720, 1660 and 1640. Then, the crude imine containing EDTA (2.5 mg) was dissolved in methanol (10 cm^3), to which 30% aqueous H_2O_2 (0.5 cm^3) was added. After the mixture had been stirred at 20 °C for 1 h it was worked up and the crude products were subjected to column chromatography on silica gel (elution with benzene). The dioxazolidine **7ea** was isolated (98 mg, 43%).

Acknowledgements

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