

[3 + 2] Cycloadditions of Carbonyl Oxides to Imines: An Alternative Approach to the Synthesis of 1,2,4-Dioxazolidines

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Carbonyl oxides, derived from the ozonolysis of vinyl ethers, readily undergo [3 + 2] cycloadditions with imines, affording the corresponding 1,2,4-dioxazolidines **6a–z** in the isolated yields of 14–97%. High degrees of stereoselectivity are observed in certain cases, suggesting that this [3 + 2] cycloaddition proceeds by a concerted process. In competition experiments, a relative order of reactivity towards carbonyl oxides was tentatively deduced: nitrene > imine > thioketone > carbonyl compound. The structure of the 1,2,4-dioxazolidine **6d** was unambiguously determined by the X-ray crystallographic analysis. 1,2,4-Dioxazolidines were found to undergo ring cleavage reactions on either thermolysis or treatment with base.

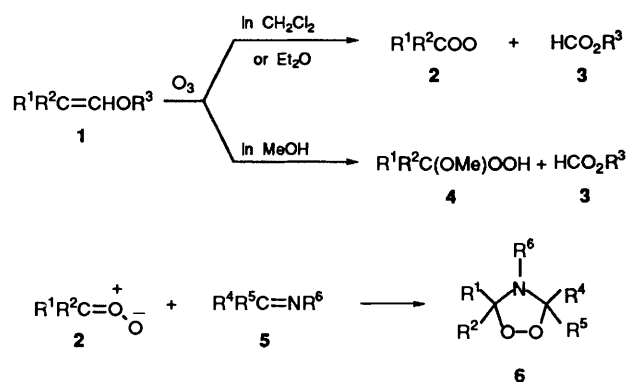
Carbonyl oxides, key intermediates in the ozonolysis of olefins,¹ readily participate as 1,3-dipoles in [3 + 2] cycloadditions to (a) carbonyl compounds (usually simple aldehydes and ketones, though, in certain circumstances, also carboxylic acid derivatives²) to give the corresponding 1,2,4-trioxolanes (ozonides); (b) olefins to give 1,2-dioxolanes,³ and (c) thioketones to give 1,2,4-dioxathiolanes.⁴ In addition, we have discovered that [3 + 2] cycloadditions of carbonyl oxides to imines represent useful synthetic routes to 1,2,4-dioxazolidines.^{5,6} We now report in detail the results of our synthetic and mechanistic studies of this cycloaddition.

Results and Discussion

Reactions of Carbonyl Oxides with Imines.—A solution of the appropriate vinyl ether **1** (2 mmol) and the imine **5** (2 mmol) in CH₂Cl₂ (20 cm³) was ozonized at –70 °C. The resulting products were isolated by trituration with methanol, or by rapid column chromatography on silica gel. In general, the reactions were clean; ¹H NMR spectra of the crude product mixture showed the presence of only the adduct **6** together with unreacted imine **5**. Although most 1,2,4-dioxazolidines **6** were stable on silica gel, the 3,4,5-trisubstituted derivatives **6n–q** tended to decompose during column chromatography (see footnote g in Table 1),^{6a} affording a complex mixture of products including the corresponding aldehyde (Scheme 1 and Table 1).

In a non-participating solvent like CH₂Cl₂, the carbonyl oxides **2**, generated *in situ* by selective ozonolysis of vinyl ethers,^{†-3a} reacted preferentially with the imines **5** to yield the corresponding 1,2,4-dioxazolidines **6**. Repeating the reactions with the vinyl ethers **1a** or **1b** and *N*-phenyldiphenylmethanimine **5a** in methanol, a known participating solvent, resulted in the quantitative recovery of the imine **5a**. In the latter case, the α -methoxy hydroperoxide **4b** was also isolated.^{2a}

The steric bulk of the α -substituents did not appear to diminish the reactivity of the imines **5** because the isolated yields of the 1,2,4-dioxazolidines **6** obtained from the reactions involving α,α,N -trisubstituted imines were generally higher than those involving α,N -disubstituted derivatives. These figures



may, however, reflect in part the differences in relative stability between 3,3,4,5-tetrasubstituted and 3,4,5-trisubstituted derivatives (see footnote g in Table 1). In contrast, the reactivity of the carbonyl oxides **2** is strongly affected by structure with marked differences in reactivity between aldehyde and ketone *O*-oxides. As indicated by the data in Table 1, aldehyde *O*-oxides **2a–c** underwent cycloaddition to a variety of imines yielding the corresponding 1,2,4-dioxazolidines in each case, whereas the sterically more encumbered ketone *O*-oxides **2d** and **2e**, derived from the ozonolyses of 1,1-diphenyl-2-methoxyethene **1d** and methoxymethylidenecyclohexane **1e** respectively, were unreactive towards imines **5e**, **g** and **p**. This suggests that the approach of the carbonyl oxide carbon to the nitrogen atom of the imine is sensitive to steric hindrance. Nonetheless, benzophenone *O*-oxide **2d** and cyclohexanone *O*-oxide **2e** did react with the highly reactive dipolarophile, 3,4-dihydroisoquinoline **5r**, affording the corresponding adducts, **6x** and **6y**, in yields of 63% and 60%, respectively (Scheme 2).

Although cycloadditions involving unsymmetrically substituted imines and carbonyl oxides would be expected to give rise to the 3,4,5-trisubstituted dioxazolidines **6i–s** as mixtures of stereoisomers, only the dioxazolidines **6k–o**, **q** and **r** were actually obtained as isomeric mixtures. Structural assignments were made by analogy with ¹H NMR spectroscopic correlations previously derived for the corresponding phenyl-substituted ozonides,^{2c} in which the ring protons of *cis*-diphenyl isomers were presumed to exhibit higher field resonances in

† The reaction between imines and ozone is very slow; the rate constant for the ozonation of *N*-phenylphenylmethanimine is 10⁴ times smaller than that of styrene.⁷

Table 1 Ozonolysis of a vinyl ether in the presence of an imine^a

Vinyl ether	Imine	1,2,4-dioxazolidine (% yield) ^b	<i>cis/trans</i> ^c	Recovered adduct 5 , % ^j
1a	5a	6a (78) ^e		
1a	5b	6b (57)		13
1a	5d	6c (68) ^e		23
1b	5a	6d (58)		
1b	5c	6e (69)		
1b	5d	6f (62) ^{e,f}		23
1b	5e	6g (82)		
1b	5f	6h (91)		
1b	5g ^d	6i (61) ^{e,f}		32
1b	5h ^d	6j (54) ^{e,f}		30
1b	5i ^d	6k (29)	75:25	
1b	5j ^d	6l (45) ^g	63:27	30
1b	5k ^d	6m (47) ^g	79:21	
1b	5l ^d	6n (22) ^g	80:20	
1b	5m ^d	6o (20) ^g	81:19	
1b	5n ^d	6p (14) ^{f,g}		58
1b	5o ^d	6q (25) ^g	78:22	
1b	5p ^d	6r (32) ^g	74:26	
1b	5q ^d	6s (69) ^f		
1c	5a	6t (51)		30
1c	5c	6u (72)		
1c	5d	6v (59) ^h		31
1c	5e	6w (97)		
1c	5g ^d	6s (49) ^f		49
1c	5j ^d	6r (35) ^g	64:36	
1d	5r ^d	6x (63)		
1e	5r ^d	6y (60)		
1c	(<i>Z</i>)- 5s ^d	6z (63)	93:7	
1c	5s ^{d,i}	6z (63)	50:50	
1f	(<i>Z</i>)- 5s ^d	6zz (80)	85:15	
1f	5s ^{d,i}	6zz (45)	50:50	

^a The reaction of a 1:1 mixture of a vinyl ether and an imine with 1 equiv. of ozone in CH₂Cl₂ at -70 °C. The dioxazolidine was isolated by column chromatography on silica gel, unless otherwise noted. ^b Isolated yield. ^c The ratio was determined from the ¹H NMR spectra of the crude products. ^d Reaction in diethyl ether. ^e Isolated by trituration with methanol. ^f Only one isomer was obtained. ^g The yield of the dioxazolidine determined from the ¹H NMR spectra of the crude products was as follows: **6l** (56); **6m** (55); **6n** (35); **6o** (50); **6p** (24); **6q** (64); **6r** (38). ^h A mixture of two stereoisomers, the ratio being *ca.* 1:1. ⁱ The reaction in the presence of a 1:1 mixture of (*E*)- and (*Z*)-**5s**. ^j Unless otherwise shown, the percentage of the recovered imine was not determined.

the ¹H NMR spectrum than the corresponding *trans*-isomers.* These assignments were further supported by ¹H NMR spectral data reported for *N*-benzyl-3,5-diphenyl-1,2,4-dioxazolidine; the *cis*-isomer exhibited two singlets at δ 5.67 (1 H) and 4.10 (1 H) whereas the *trans*-isomer exhibited a singlet at δ 5.89 (2 H) and an AB quartet (2 H) for the diastereotopic *N*-benzyl protons at δ 3.70 and 3.78 (*J* 13).^{6a} Analysis of the crude product mixtures by ¹H NMR spectroscopy indicated that the *cis*-dioxazolidine was invariably the major stereoisomer (Table 1).[†]

Assuming that the carbonyl oxide and imine component have the *anti*- and *E*-configurations respectively, examination of possible transition states for concerted [3 + 2] cycloaddition processes leading to the *cis*- and *trans*-isomers suggests that in

the latter case, there would be a sterically unfavourable eclipsing interaction between the substituent of carbonyl oxide and the *N*-substituent of the imine (Fig. 1). Consistent with this, the dioxazolidines **6i**, **j**, **p** and **s** derived from the cycloaddition with the imines having bulkier *N*-substituents (phenyl or cyclohexyl), were obtained as single isomers.

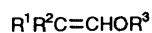
Cycloaddition of carbonyl oxide **2b** to the configurationally stable (*Z*)-*N*-methyl-(4-chlorophenyl)phenylmethanimine **5s** was also found to be highly stereoselective, yielding the corresponding dioxazolidine **6z** as a 93:7 isomeric mixture. Attempted separation of these isomers by either column chromatography on silica gel or recrystallisation from methanol, resulted in substantial rearrangement of the major isomer to the minor one, thereby providing 2:1 and 1:1 mixtures of two stereoisomers, respectively. The ozonolysis of the vinyl ether **1f** in the presence of (*Z*)-**5s** resulted in the formation of 80% yield of compound **6zz** as a 85:15 isomeric mixture.

Since [3 + 2] cycloadditions between carbonyl oxides and vinyl ethers are highly stereospecific, it has been suggested that such reactions are also concerted.^{1d} The stereochemical evidence obtained thusfar is also consistent with the notion that the analogous [3 + 2] cycloadditions between carbonyl oxides and imines are also concerted processes. In non-concerted [3 + 3] cycloadditions between carbonyl oxides and either (*E*)- or (*Z*)-*N*-(α -tolylbenzylidene)methylamine *N*-oxide, 1:1 mixtures of the stereoisomeric cycloadducts are generally obtained.⁸

Reactions of Carbonyl Oxides with Competing Reactants.—In addition to carbonyl compounds and imines, carbonyl oxides

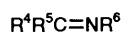
* By analogy with 3,5-dialkyl-1,2,4-trioxolane,^{2e} the *cis*-isomer of 3,5-dialkyl-1,2,4-dioxazolidine was, however, assigned the lower field methine proton resonance. Consistent with this, integration of the peak for the methine protons in 3-alkyl-5-phenyl-1,2,4-dioxazolidine revealed that the peak with the lower field δ value for the proton at the carbon bearing the alkyl substituent consistently corresponded to the peak with the higher field δ value for the proton at the phenyl-substituted carbon.

[†] Schaap and co-workers^{6a} have discovered that DCA-sensitized photooxygenation of *cis*- and *trans*-2,3-diphenylaziridine in acetonitrile yields a *cis*-*trans* mixture of 3,5-diphenyl-1,2,4-dioxazolidine, the *cis*:*trans* ratio being remarkably influenced by the steric bulk of the *N*-substituent R (for example R = H, *cis*:*trans* ratio = 100:0; R = *tert*-butyl, *cis*:*trans* ratio = 0:100).



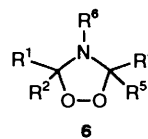
1

- a $R^1 = R^2 = H, R^3 = CH_2CHMe_2$
 b $R^1 = Ph, R^2 = H, R^3 = Me$
 c $R^1 = [CH_2]_6Me, R^2 = H, R^3 = Me$
 d $R^1 = R^2 = Ph, R^3 = Me$
 e $R^1, R^2 = -[CH_2]_5-, R^3 = Me$
 f $R^1 = cyclohexyl, R^2 = H, R^3 = Me$



5

- a $R^4 = R^5 = R^6 = Ph$
 b $R^4 = R^5 = Ph, R^6 = tert\text{-butyl}$
 c $R^4 = R^5 = Ph, R^6 = H$
 d $R^4 = R^5 = Ph, R^6 = Me$
 e $R^4, R^5 = -[CH_2]_5-, R^6 = Ph$
 f $R^4, R^5 = -CH_2CH_2CH(CMe_3)CH_2CH_2-, R^6 = Ph$
 g $R^4 = R^5 = Ph, R^6 = H$
 h $R^4 = 4\text{-ClC}_6\text{H}_4, R^5 = H, R^6 = Ph$
 i $R^4 = Ph, R^5 = H, R^6 = Me$
 j; $R^4 = Ph, R^5 = H, R^6 = CH_2Ph$
 k; $R^4 = 2\text{-CF}_3\text{C}_6\text{H}_4, R^5 = H, R^6 = CH_2Ph$
 l; $R^4 = Ph, R^5 = H, R^6 = hexyl$
 m; $R^4 = Ph, R^5 = H, R^6 = cyclohexylmethyl$
 n; $R^4 = Ph, R^5 = H, R^6 = cyclohexyl$
 o; $R^4 = cyclohexyl, R^5 = H, R^6 = CH_2Ph$
 p; $R^4 = heptyl, R^5 = H, R^6 = CH_2Ph$
 q; $R^4 = heptyl, R^5 = H, R^6 = Ph$
 s; $R^4 = 4\text{-ClC}_6\text{H}_4, R^5 = Ph, R^6 = Me$



6

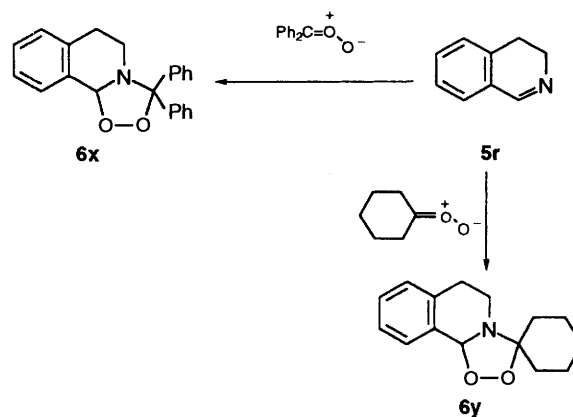
- a $R^1 = R^2 = H, R^4 = R^5 = R^6 = Ph$
 b $R^1 = R^2 = H, R^4 = R^5 = Ph, R^6 = tert\text{-butyl}$
 c $R^1 = R^2 = H, R^4 = R^5 = Ph, R^6 = Me$
 d $R^4 = Ph, R^2 = H, R^4 = R^5 = R^6 = Ph$
 e $R^1 = Ph, R^2 = H, R^4 = R^5 = Ph, R^6 = H$
 f $R^1 = Ph, R^2 = H, R^4 = R^5 = Ph, R^6 = Me$
 g $R^1 = Ph, R^2 = H, R^4, R^5 = -[CH_2]_5-, R^6 = H$
 h $R^1 = Ph, R^2 = H, R^4, R^5 = -CH_2CH_2CH(CMe_3)CH_2CH_2-, R^6 = Ph$
 l $R^1 = Ph, R^2 = H, R^4 = R^5 = Ph, R^6 = H$
 j $R^1 = Ph, R^2 = H, R^4 = 4\text{-ClC}_6\text{H}_4, R^5 = H, R^6 = Ph$
 k $R^1 = Ph, R^2 = H, R^4 = Ph, R^5 = H, R^6 = Me$
 l $R^1 = Ph, R^2 = H, R^4 = Ph, R^5 = H, R^6 = CH_2Ph$
 m $R^1 = Ph, R^2 = H, R^4 = 2\text{-CF}_3\text{C}_6\text{H}_4, R^5 = H, R^6 = CH_2Ph$
 n $R^1 = Ph, R^2 = H, R^4 = Ph, R^5 = H, R^6 = hexyl$
 o $R^1 = Ph, R^2 = H, R^4 = Ph, R^5 = H, R^6 = cyclohexylmethyl$
 p $R^1 = Ph, R^2 = H, R^4 = Ph, R^5 = H, R^6 = cyclohexyl$
 q $R^1 = Ph, R^2 = H, R^4 = cyclohexyl, R^5 = H, R^6 = CH_2Ph$
 r $R^1 = Ph, R^2 = H, R^4 = heptyl, R^5 = H, R^6 = CH_2Ph$
 s $R^1 = Ph, R^2 = H, R^4 = heptyl, R^5 = H, R^6 = Ph$
 t $R^1 = [CH_2]_6Me, R^2 = H, R^4 = R^5 = R^6 = Ph$
 u $R^1 = [CH_2]_6Me, R^2 = H, R^4 = R^5 = Ph, R^6 = H$
 v $R^1 = [CH_2]_6Me, R^2 = H, R^4 = R^5 = Ph, R^6 = Me$
 w $R^1 = [CH_2]_6Me, R^2 = H, R^4, R^5 = -[CH_2]_5-, R^6 = Ph$
 x $R^1, R^6 = -o\text{-C}_6\text{H}_4[CH_2]_2-, R^2 = H, R^4 = R^5 = Ph$
 y $R^1, R^6 = -o\text{-C}_6\text{H}_4[CH_2]_2-, R^2 = R^3 = H, R^4, R^5 = -[CH_2]_5-$
 z $R^1 = Ph, R^2 = H, R^4 = 4\text{-ClC}_6\text{H}_4, R^5 = Ph, R^6 = Me$
 zz $R^1 = 4\text{-ClC}_6\text{H}_4, R^2 = Ph, R^4 = cyclohexyl, R^5 = H, R^6 = Me$

are known to form cycloadducts with a variety of other compounds including thioadamantanone⁴ and nitrones.⁸ It was of interest to establish, at least qualitatively, an order of relative reactivity for imines in comparison to these other carbonyl oxide trapping reagents. The results obtained are summarised in Table 2.

When the ozonolysis of the vinyl ether **1a** was carried out in the presence of an equimolar mixture of benzophenone **7a** and the imine **5b** in CH_2Cl_2 at $-70^\circ C$, 3,3-diphenyl-1,2,4-trioxolane **9a** and the dioxazolidine **6b** were obtained in yields of 3% and 46%, respectively. A similar result was noted for the analogous competition experiment between cyclohexanone **7d** and cyclohexylideneaniline **5e**. With benzaldehyde **7e** and benzylbenzylideneamine **5j** and carbonyl oxide **2b**, the difference in yield between stilbene ozonide **9b** and the dioxazolidine **6l** was less marked than above (22% and 44%, respectively) indicating that the reactivities of these two dipolarophiles were less dissimilar.

Since the competition experiment between 2-(trifluoromethyl)benzaldehyde **7f** and the imine **5k** with carbonyl oxide **2b** yields the ozonide **9c** (70% yield) as the sole isolable product, whereas a similar experiment involving an equimolar mixture of imines **5j** and **5k** gave a 1 : 1 mixture of the 1,2,4-dioxazolidines **6l** and **6m** (35% yield for each) (Table 2), it appears that substituent electronic effects have a more pronounced influence on the reactivity of carbonyl compounds than imines.*

The results of competition experiments involving adamantanone **7g** and related compounds, adamantylidenebenzylamine **5t** and thioadamantanone **10** (Scheme 3 and Table 2) suggest that the order of reactivity follows the sequence: **5t** > **10** > **7g**.



Scheme 2

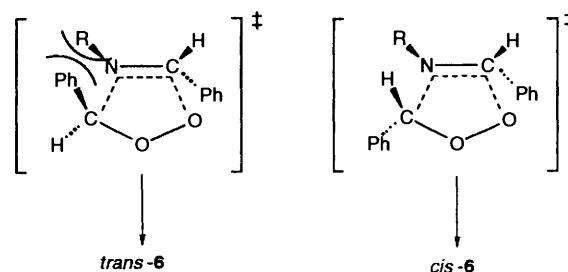


Fig. 1

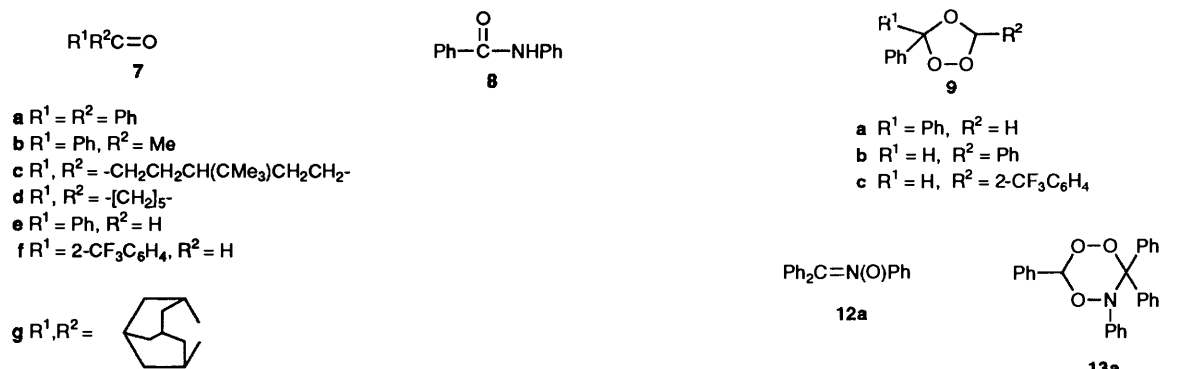
* Electron-withdrawing substituents are observed to increase significantly the reactivity of the carbonyl compounds towards carbonyl oxides.^{1,2e} e.g. in competition experiments, 2-(trifluoromethyl)benzaldehyde **7f** was found to be ca. 8 times more reactive than benzaldehyde **7e** towards benzaldehyde *O*-oxide **2b**.^{2a}

Comparison of the relative reactivities of imines and nitrones were not entirely conclusive. On one hand, the ozonolysis of compound **1b** in the presence of an equimolar mixture of the imine **5a** and *N*-(α -phenylbenzylidene)phenylamine *N*-oxide **12a** in CH_2Cl_2 at $-70^\circ C$ afforded the

Table 2 Competitive reactions between two different trapping reagents^a

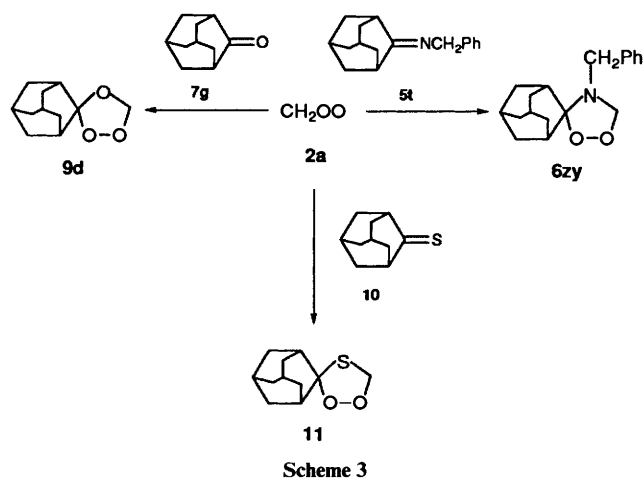
Vinyl ether (mmol)	Trapping reagents (mmol)	O ₃ (mmol)	Solvent	Products (% yield)
1b (1)	5a (1), 5e (1)	1	CH ₂ Cl ₂	6g (79)
1b (1)	5j (1), 5k (1)	1	diethyl ether	6l (35), 6m (35)
1a (1)	5b (1), 7a (1)	1	CH ₂ Cl ₂	6b (46), 9a (3)
1b (1)	5e (1), 7d (1)	1	CH ₂ Cl ₂	6g (80)
1b (1)	5j (1), 7e (1)	1	diethyl ether	6l (44), 9b (22)
1b (2)	5j (1), 7e (1)	2	diethyl ether	6l (85), 9b (42)
1b (1)	5k (1), 7f (1)	1	diethyl ether	9c (70)
1b (2)	5k (1), 7f (1)	2	diethyl ether	6m (50), 9c (95)
1a (2)	5t (1), 10 (1)	2	diethyl ether	6zy (82), 11 (58)
1a (2)	5t (1), 7g (1)	2	diethyl ether	6zy (90)
1a (2)	7g (1), 10 (1)	1	diethyl ether	11 (75)
1b (1)	5a (1), 12a (1)	1	CH ₂ Cl ₂	13a (57)
1b (1)	5j (1), 12b (1)	1	CH ₂ Cl ₂	6l (25), 13b (27)
1b (1)	7e (4), 7f (1)	1	CH ₂ Cl ₂	9b (13), 9c (25) ^b

^a The reaction of a mixture of a vinyl ether and two dipolarophiles at -70 °C. ^b Taken from the data in reference 2a.



1,2,4,5-trioxazine **13a**, derived from capture of the nitron **12a** by benzaldehyde *O*-oxide **2b** (57% yield), whereas the analogous reaction involving the imine **5j** and the nitron **12b** gave the dioxazolidine **6l** and 5-benzyl-3,6-diphenyl-dihydro-1,2,4,5-trioxazine **13b** in yields of 25% and 27%, respectively (Table 2). It is surprising that the reaction between carbonyl oxides and nitrones, which must be stepwise, should be at least as fast as that involving imines, which is likely to be concerted.

Although there are anomalies arising from substituent electronic and steric effects, the results from the competition experiments suggest an order of reactivity towards carbonyl oxides: nitrones ≥ imines > thioketones > carbonyl compounds.



X-Ray Crystal Structure of Dioxazolidine 6d.—Although the adducts **6** could be characterized by elemental analysis and ¹H-¹³C NMR spectra, it was important to establish unambiguously the nature of the ring system. The structure of the adduct **6a** had been determined previously by X-ray crystallography.⁵ Since compound **6d** also afforded suitable single crystals, a second opportunity was therefore provided to investigate the structural features of this relatively uncommon ring system.

The crystal structure consists of well separated molecules of compound **6d** (no significant intermolecular contacts within 3.5 Å). As depicted in Fig. 2, compound **6d** was confirmed as being a 1,2,4-dioxazolidine derivative. The central 1,2,4-dioxazolidine ring of compound **6d** adopts a slightly distorted envelope conformation in which the oxygen atom O(1), distal from the geminal phenyl groups at C(1), lies out-of-plane; deviations from a least squares plane through atoms O(2), C(1), N(1) and C(2) are within ±0.05 Å and O(1) lies 0.703 Å out of the plane. The angle between the planes O(2)-C(1)-N(1)-C(2) and O(2)-O(1)-C(2) is 48.8° (*cf.* 45.5° for corresponding interplanar angle in **6a**⁵). The geminal phenyl groups at C(1) adopt pseudo axial and equatorial positions and the phenyl group at C(2) is in an equatorial position, presumably to minimize steric interactions. The geometry at the ring nitrogen atom N(1) is pyramidal with the phenyl ring atom

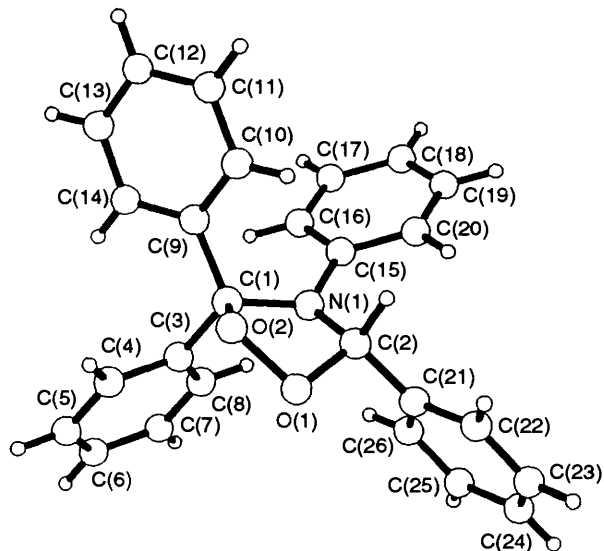


Fig. 2 Solid state molecular structure of the 1,2-dioxazolidine **6d** as determined by X-ray crystallographic analysis

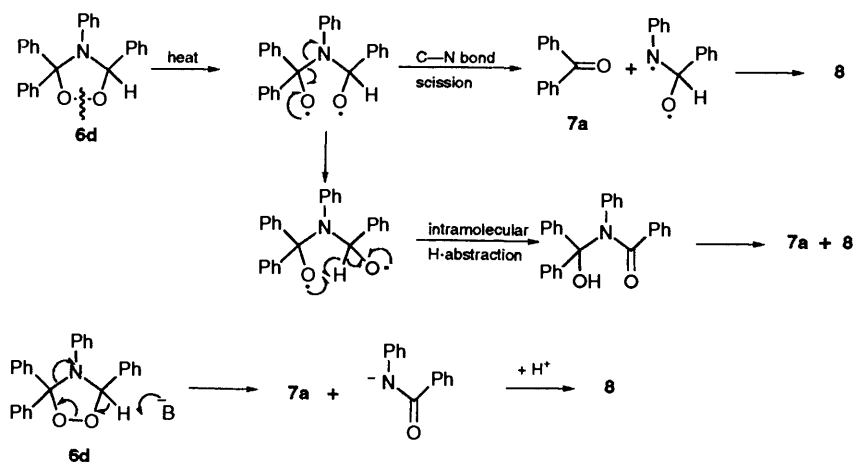
C(15) making an angle of 28.9° with the plane O(2)–C(1)–N(1)–C(2).

There is good agreement between the corresponding bond lengths and angles around the 1,2,4-dioxazolidine ring in both compounds **6d** and **6a**, and, in general, the observed values lie within expected ranges, e.g. the O–O bond length [1.477(3) Å] is typical for 5- and 6-membered cyclic peroxides.⁹

Decomposition Reactions of the 1,2,4-Dioxazolidines 6.—The dioxazolidines **6** were generally found to be thermally stable below 100°C . Thermolysis of a solution of compound **6d** in benzene at 130°C afforded a clean thermolysate composed of benzophenone **7a** and benzanilide **8** in quantitative yield. The formation of these products would be consistent with a radical mechanism involving an initial O–O homolysis followed by two plausible hydrogen abstraction or scission pathways as outlined in Scheme 4.

Treatment of the dioxazolidine **6d** with triphenylphosphine resulted in deoxygenation of the system with concomitant formation of benzophenone **7a** and the imine **5g** in quantitative yield.

Base-catalysed decomposition of compound **6d** afforded quantitatively benzophenone **7a** and benzanilide **8**.



Scheme 4

Table 3 Decomposition of 1,2,4-dioxazolidine

Dioxazolidine	Condition	Products (% yield)
6d	PPh_3^a	5g (100), 7a (100) ^f
6d	heat ^b	7a (100), 8 (100)
6d	LDA ^c	7a (63), 8 (65)
6d	TFA ^d	7a (100)
6f	PPh_3^a	5g (100), 7b (100) ^f
6f	heat ^b	7b (56), 8 (53)
6f	LDA ^c	7b (57), 8 (60)
6f	TFA ^d	7b (91)
6h	PPh_3^a	5g (90), 7c (93) ^f
6h	Et_3N^e	7c (90), 8 (95)

^a Treatment with 1 equiv. of PPh_3 in CDCl_3 at room temp. for 24 h. ^b Thermolysis in benzene in a sealed tube at 130°C for 5 h. ^c Treatment with 1 equiv. of LDA (lithium diisopropylamide) in tetrahydrofuran at 0°C for 30 min. ^d Treatment with 2 equiv. of TFA (trifluoroacetic acid) in methylene dichloride at room temp. for 40 min. ^e Treatment with 1 equiv. of triethylamine in benzene at room temp. for 24 h. ^f Determined by ^1H NMR spectroscopic analysis.

Similar results were observed for the decomposition reactions of dioxazolidines **6f**, **h** (Table 3). The patterns of ring fragmentation on thermal or induced decomposition are broadly in agreement with those previously reported for other 1,2,4-dioxazolidines^{6c–e} and also for 1,2,4-trioxanes.¹⁰

Experimental

General.— ^1H - and ^{13}C -NMR spectra were recorded on JEOL JNM-PS-100 and JNM-GSX-400 spectrometers, respectively, with CDCl_3 as the solvent (unless otherwise stated). J values are given in Hz. Mass spectral data were obtained with a Hitachi RMU-6H spectrometer and IR with a Hitachi 215 spectrometer.

Ozone was generated using a Nippin Ozone ON-I-2 Ozonator ($50\text{ dm}^3\text{ h}^{-1}\text{ O}_2$). Silica gel YMC-Gel (70-230 mesh) was used for column chromatography.

The imines **5a**,¹¹ **5b**,¹² **5c**,¹³ **5d**,¹⁴ **5e**,¹⁴ **5f**,¹⁵ **5g**,¹⁶ **5h**,¹⁷ **5i**,¹⁸ **5j**,¹⁹ **5k**,¹⁹ **5l**,²⁰ **5m**,¹⁹ **5n**,²¹ **5o**,²² **5p**,¹⁹ **5q**,¹⁶ **5r**,²³ **5s**,²⁴ **5t**¹⁴ were prepared by the reported literature methods.

CAUTION: since organic ozonides and peroxides are potentially hazardous compounds, they must be handled with due care; avoid exposure to strong heat, light, mechanical shock, oxidisable organic materials or transition metal ions. No particular difficulties were experienced in handling any of the new organic ozonides or peroxides synthesised in this work

using the reaction scales and procedures described below, together with the safeguards mentioned above.

(*Z*)-*N*-Methyl(4-Chlorophenyl)phenylmethanimine (**5s**).²⁴ —M.p. 90–91 °C (from diethyl ether–hexane); δ_{H} 3.17 (3 H, s) and 6.9–7.9 (9 H, m); δ_{C} 41.50, 128.10, 128.12, 128.86, 129.29, 130.03, 134.42, 134.74, 139.46 and 168.45.

Imine 5s. A 1 : 1 mixture of *E*- and *Z*-isomer²⁴ was an oil; b.p. 130–132 °C (2 mmHg); δ_{H} 3.17 (3 H, s) and 6.9–7.9 (9 H, m); δ_{C} 41.42, 127.62, 128.02, 128.14, 128.45, 128.52, 128.55, 128.77, 129.21, 129.39, 129.80, 129.93, 131.33, 135.77, 135.86, 138.22, 139.39, 168.29 and 168.33.

Ozonolysis of a Vinyl Ether in the Presence of an Imine in CH₂Cl₂ or in Diethyl Ether.—Ozonolysis of a mixture containing isobutyl vinyl ether **1a** and *N*-phenyldiphenylmethanimine **5a** in CH₂Cl₂ is representative. To a solution of compounds **1a** (2 mmol) and **5a** (2 mmol) in CH₂Cl₂ (20 cm³), was passed a slow stream of ozone (2 mmol) at –70 °C. After evaporation of the solvent under reduced pressure, the residue was triturated with methanol to give 3,3,4-triphenyl-1,2,4-dioxazolidine **6a**. For the method of isolation of other dioxazolidines, see the footnote in Table 1.

3,3,4-Triphenyl-1,2,4-dioxazolidine **6a**. M.p. 107–108 °C (from ethyl acetate) (Found: C, 79.0; H, 5.7; N, 4.6; *M*⁺, 303. C₂₀H₁₇NO₂ requires C, 79.21; H, 5.61; N, 4.62%; *M*, 303); δ_{H} 5.39 (2 H, s), 6.5–7.1 (5 H, m) and 7.2–7.5 (10 H, m); δ_{C} 85.48, 101.28, 118.01 (2 C), 120.69, 128.08–128.89 (12 C), 138.35 (2 C) and 143.83; ν_{max} (KBr)/cm^{–1} 1590, 1492, 1471, 1440, 1360, 1338, 1227, 1200, 1178, 1139, 1096, 1074, 1032, 749, 734, 709 and 685.

4-tert-Butyl-3,3-diphenyl-1,2,4-dioxazolidine **6b**. M.p. 125–127 °C (from ethyl acetate–hexane) (Found: C, 75.8; H, 7.4; N, 4.9. C₁₈H₂₁NO₂ requires C, 76.33; H, 7.42; N, 4.95%; δ_{H} 1.05 (9 H, s), 4.99 (2 H, s) and 7.2–7.7 (10 H, m); ν_{max} (KBr)/cm^{–1} 2970, 1480, 1450, 1400, 1369, 1260, 1213, 1192, 1103, 1020, 750 and 704.

3-Methyl-3,4-diphenyl-1,2,4-dioxazolidine **6c**. Oil (Found: C, 74.6; H, 6.3; N, 5.7. C₁₅H₁₅NO₂ requires C, 74.69; H, 6.22; N, 5.81%; δ_{H} 1.46 (3 H, s), 4.82 (1 H, d, *J* 4), 5.05 (1 H, d, *J* 4) and 6.9–7.6 (10 H, m).

3,3,4,5-Tetraphenyl-1,2,4-dioxazolidine **6d**. M.p. 144–145 °C (decomp.) (from ethyl acetate) (Found: C, 82.3; H, 5.4; N, 3.7. C₂₆H₂₁NO₂ requires C, 82.32; H, 5.54; N, 3.69%; δ_{H} 6.62 (1 H, s), 6.3–6.9 (5 H, m) and 7.2–7.8 (15 H, m); ν_{max} (KBr)/cm^{–1} 1608, 1583, 1505, 1457, 1380, 1330, 1295, 1239, 1213, 1200, 1188, 1138, 1090, 1065, 756, 733 and 699.

3,3,5-Triphenyl-1,2,4-dioxazolidine **6e**. Oil (Found: C, 79.9; H, 5.9; N, 4.3. C₂₀H₁₇NO₂ requires C, 79.21; H, 5.61; N, 4.62%; δ_{H} 3.79 (1 H, d, *J* 11), 5.66 (1 H, d, *J* 11) and 7.1–7.8 (15 H, m); ν_{max} (Neat)/cm^{–1} 1594, 1489, 1488, 1358, 1310, 1209, 1106, 1065, 1023, 743 and 691.

3-Methyl-3,4,5-triphenyl-1,2,4-dioxazolidine **6f**. M.p. 125–126.5 °C (decomp.) (from ethyl acetate–hexane) (Found: C, 79.4; H, 6.1; N, 4.4. C₂₁H₁₉NO₂ requires C, 79.50; H, 5.99; N, 4.42%; δ_{H} 2.29 (3 H, s), 6.47 (1 H, s), 6.3–7.1 (5 H, m) and 7.2–7.7 (10 H, m); ν_{max} (KBr)/cm^{–1} 1595, 1497, 1446, 1373, 1321, 1300, 1283, 1258, 1206, 1160, 1102, 1069, 1020, 743 and 688.

3,4-Diphenyl-1,2-dioxo-4-azaspiro[5.4]decane **6g**. M.p. 71–73 °C (from methanol) (Found: C, 77.0; H, 7.2; N, 4.7. C₁₉H₂₁NO₂ requires C, 77.29; H, 7.12; N, 4.75%; δ_{H} 1.1–2.5 (10 H, m), 6.22 (1 H, s), 6.8–6.9 (3 H, m) and 7.1–7.6 (7 H, m); ν_{max} (KBr)/cm^{–1} 2937, 2850, 1592, 1490, 1446, 1340, 1291, 1270, 1200, 1162, 1071, 1048, 1021, 763, 737 and 688.

8-tert-Butyl-3,4-diphenyl-1,2-dioxo-4-azaspiro[5.4]decane **6h**. Oil (Found: C, 78.9; H, 8.3; N, 4.1. C₂₃H₂₉NO₂ requires C, 78.63; H, 8.26; N, 3.99%; δ_{H} 0.87 (9 H, s), 1.1–2.5 (9 H, m), 6.1 (1 H, s) and 6.7–7.5 (10 H, m).

3,4,5-Triphenyl-1,2,4-dioxazolidine **6i**. M.p. 163–164 °C (from ethyl acetate–hexane) (Found: C, 78.9; H, 5.6; N, 4.6. C₂₀H₁₇NO₂ requires C, 79.21; H, 5.61; N, 4.62%; δ_{H} 6.51 (2 H, s), 6.3–7.2 (5 H, m) and 7.3–7.5 (10 H, m); ν_{max} (KBr)/cm^{–1} 1597, 1570, 1503, 1450, 1386, 1363, 1330, 1290, 1203, 1138, 1080, 1065, 1047, 1020, 742 and 685.

5-(4-Chlorophenyl)-3,4-diphenyl-1,2,4-dioxazolidine **6j**. M.p. 126.5–127 °C (from ethyl acetate–hexane) (Found: C, 70.9; H, 4.8; N, 4.1. C₂₀H₁₆ClNO₂ requires C, 71.11; H, 4.74; N, 4.15%; δ_{H} 6.48 (2 H, s), 6.3–7.2 (5 H, m) and 7.3–7.5 (9 H, m); ν_{max} (KBr)/cm^{–1} 1600, 1572, 1505, 1440, 1368, 1213, 1165, 1080, 1009 and 740.

4-Benzyl-3-phenyl-5-[2-(trifluoromethyl)phenyl]-1,2,4-dioxazolidine **6m**. Oil (a *cis*:*trans* mixture of 71 : 29); δ_{H} 3.69 (s, CH₂, minor), 4.07 (s, CH₂, major), 5.58 (s, CH, major), 5.82 (s, CH, minor), 6.00 (br s, CH, major), 6.06 (br s, CH, minor) and 7.0–8.0 (14 H, m).

4-Hexyl-3,5-diphenyl-1,2,4-dioxazolidine **6n**. Oil (a *cis*:*trans* mixture of 63 : 37); δ_{H} 0.7–1.5 (11 H, m), 2.8–3.0 (2 H, m), 5.52 (s, CH, major), 5.58 (s, CH, minor) and 7.2–7.7 (10 H, m).

4-(Cyclohexylmethyl)-3,5-diphenyl-1,2,4-dioxazolidine **6o**. Oil (a *cis*:*trans* mixture of 81 : 19); δ_{H} 0.5–1.9 (10 H, m), 2.75 (2 H, d, *J* 6), 5.51 (s, CH, major), 5.88 (s, CH, minor) and 7.2–7.7 (10 H, m).

4-Cyclohexyl-3,5-diphenyl-1,2,4-dioxazolidine **6p**. M.p. 108–109 °C (Found: C, 77.5; H, 7.5; N, 4.5. C₂₀H₂₃NO₂ requires C, 77.67; H, 7.44; N, 4.53%; δ_{H} 1.1–2.1 (10 H, m), 2.7–3.0 (1 H, m), 5.79 (2 H, s) and 7.2–7.7 (10 H, m).

4-Benzyl-3-cyclohexyl-5-phenyl-1,2,4-dioxazolidine **6q**. Oil (a *cis*:*trans* mixture of 78 : 22); δ_{H} 0.6–2.0 (10 H, m), 3.99 (2 H, s), 4.44 (1 H, d, *J* 7.5), 5.54 (s, CH, major), 5.82 (s, CH, minor) and 7.1–7.5 (10 H, m).

4-Benzyl-3-heptyl-5-phenyl-1,2,4-dioxazolidine **6r**. Oil (a *cis*:*trans* mixture of 74 : 26); δ_{H} 0.8–1.8 (15 H, m), 3.92 (2 H, s), 4.5–4.7 (1 H, m), 5.38 (s, CH, major), 5.64 (s, CH, minor) and 7.1–7.5 (10 H, m).

5-Heptyl-3,4-diphenyl-1,2,4-dioxazolidine **6s**. Oil (Found: C, 77.4; H, 8.5; N, 4.2. C₂₁H₂₇NO₂ requires C, 77.54; H, 8.31; N, 4.31%; δ_{H} 0.8–0.9 (3 H, m), 1.2–1.8 (12 H, m), 5.44 (1 H, dd, *J* 6 and 4.5), 5.95 (1 H, s), 6.5–6.6 (2 H, m), 6.7–6.9 (1 H, m) and 7.0–7.6 (7 H, m); ν_{max} (Neat)/cm^{–1} 2920, 2850, 1599, 1498, 1452, 1340, 1293, 1206, 1149, 1074, 1035, 743 and 688.

5-Heptyl-3,3,4-triphenyl-1,2,4-dioxazolidine **6t**. Oil (Found: C, 80.9; H, 8.0; N, 3.7. C₂₇H₃₁NO₂ requires C, 80.80; H, 7.73; N, 3.49%; δ_{H} 0.8–0.9 (3 H, m), 1.2–1.8 (12 H, m), 5.76 (1 H, dd, *J* 7 and 2), 6.5–6.8 (3 H, m) and 6.9–7.7 (12 H, m); ν_{max} (Neat)/cm^{–1} 2913, 2845, 1594, 1495, 1447, 1340, 1310, 1232, 1190, 1134, 1036, 743 and 689.

5-Heptyl-3,3-diphenyl-1,2,4-dioxazolidine **6u**. Oil (Found: C, 77.8; H, 8.4; N, 4.4. C₂₁H₂₁NO₂ requires C, 77.54; H, 8.31; N, 4.31%; δ_{H} 0.8–0.9 (3 H, m), 1.2–1.7 (12 H, m), 3.22 (1 H, d, *J* 11), 4.5–4.7 (1 H, m) and 7.1–7.6 (10 H, m).

5-Heptyl-3-methyl-3,4-diphenyl-1,2,4-dioxazolidine **6v**. Oil (a 1 : 1 *cis*:*trans* mixture) (Found: C, 77.8; H, 8.7; N, 4.2. C₂₂H₂₉NO₂ requires C, 77.88; H, 8.55; N, 4.13%; δ_{H} 0.8–0.9 (3 H, m), 1.2–1.8 (12 H, m), 1.72 (1.5 H, s), 1.75 (1.5 H, s), 5.25 (0.5 H, dd, *J* 6 and 4.5), 5.50 (0.5 H, dd, *J* 6 and 4.5), 6.6–6.9 (3 H, m) and 7.1–7.7 (7 H, m); ν_{max} (Neat)/cm^{–1} 2924, 2850, 1597, 1496, 1494, 1444, 1369, 1340, 1259, 1235, 1174, 1118, 1060, 1020, 753 and 690.

3-Heptyl-4-phenyl-1,2-dioxo-4-azaspiro[5.4]decane **6w**. Oil (Found: C, 75.8; H, 9.9; N, 4.5. C₂₀H₃₁NO₂ requires C, 75.71; H, 9.78; N, 4.42%; δ_{H} 0.8–0.9 (3 H, m), 1.2–1.9 (12 H, m), 5.24 (1 H, dd, *J* 6 and 4), 6.7–6.9 (3 H, m) and 7.1–7.2 (2 H, m).

3,3-Diphenyl-3,5,6,11-tetrahydroisoquinolo[1,2-c][1,2,4]dioxazole **6x**. M.p. 136–138 °C (from methanol) (Found: C, 80.0; H, 5.9; N, 4.3. C₂₂H₁₉NO₂ requires C, 80.23; H, 5.78; N, 4.26%; δ_{H} 2.5–3.3 (4 H, m), 5.81 (1 H, s) and 7.1–7.9 (14 H, m).

3',3'-Diphenylspiro[cyclohexane-1,3'-3',5',6',11'-tetrahydroisoquinolo[1,2-c][1,2,4]dioxazole] **6y**. M.p. 64–68 °C (from methanol) (Found: C, 73.0; H, 7.8; N, 5.8. C₁₅H₁₉NO₂ requires C, 73.47; H, 7.76; N, 5.71%); δ_{H} 1.4–2.1 (10 H, m), 2.8–3.2 (4 H, m), 5.92 (1 H, s) and 7.1–7.6 (4 H, m).

4-Benzylspiro[1,2,4-dioxazolidine-3,2'-tricyclo[3.3.1.1^{3,7}]-decane] **6zy**. M.p. 94–96 °C (from methanol) (Found: C, 75.7; H, 8.1; N, 5.0. C₁₈H₂₃NO₂ requires C, 75.79; H, 8.07; N, 4.91%); δ_{H} 1.6–2.3 (14 H, m), 3.93 (2 H, s), 4.62 (2 H, s) and 7.2–7.5 (5 H, m).

The physical properties of **6k**, **l** have been already reported by Schaap and co-workers.^{6a}

Ozonolysis of the Vinyl Ether 1a in the Presence of the Imine 5a in MeOH–CH₂Cl₂.—A solution of the vinyl ether **1a** (2 mmol) and the imine **5a** (2 mmol) in MeOH–CH₂Cl₂ (20 cm³; 1:1) was treated with 2 mmol of ozone at –70 °C. The reaction mixture was poured into water, extracted with diethyl ether and was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was recrystallized from methanol to afford the imine **5a** quantitatively.

Ozonolysis of the Vinyl Ether 1b in the Presence of (Z)-N-Methyl-(4-chlorophenyl)phenylmethanimine (Z)-5s.—To a solution of the vinyl ether **1b** (2 mmol) and the imine (Z)-**5s** (1 mmol) in diethyl ether (20 cm³), was passed a slow stream of ozone (1 mmol) at –70 °C. The solvent was partially evaporated and the precipitated solid was filtered and then was washed with methanol (211 mg, 60%). The ¹³C NMR spectra of the crude mixture of products and of the isolated solid showed the presence of a 93:7 mixture of two isomeric 3-(4-chlorophenyl)-N-methyl-3,5-diphenyl-1,2,4-dioxazolidine **6z**. M.p. 110–115 °C (Found: C, 71.8; H, 5.1; N, 4.0. C₂₁H₁₈ClNO₂ requires C, 71.68; H, 5.17; N, 3.98%); δ_{H} (major isomer) 2.10 (3 H, s), 5.57 (1 H, s) and 7.2–7.8 (14 H, m); δ_{C} 35.17, 100.36, 101.59, 128.13, 128.23, 128.41, 128.56, 128.69, 128.89, 129.54, 130.01, 133.80, 134.17, 137.66 and 141.72. Recrystallization from methanol gave a 2:1 mixture of compound **6z**. M.p. 163–164 °C (Found: C, 71.6; H, 5.0; N, 3.6. C₂₁H₁₈ClNO₂ requires C, 71.68; H, 5.17; N, 3.98%); δ_{H} (minor isomer) 2.10 (3 H, s), 5.57 (1 H, s) and 7.2–7.8 (14 H, m); δ_{C} 34.72, 99.65, 101.73, 127.94, 128.33, 128.35, 128.48, 12.64, 128.83, 129.70, 129.92, 133.77, 134.66, 137.33 and 141.53. Column chromatography on silica gel resulted in the isolation of a 1:1 mixture of *cis*- and *trans*-**6z**.

Ozonolysis of the Vinyl Ether 1f in the Presence of the Imine (Z)-5s.—A mixture of compound **1f** (2 mmol) and the imine (Z)-**5s** (1 mmol) was treated with ozone (1 mmol) in diethyl ether (20 cm³) at –70 °C. After partial evaporation of the solvent, the precipitated crystals were filtered and washed with methanol (286 mg; 80%). The ¹³C NMR spectrum showed the presence of a 85:15 mixture of two stereoisomeric dioxazolidines **6zz**. Recrystallization from methanol gave a 4:3 mixture of 3-(4-chlorophenyl)-5-cyclohexyl-N-methyl-3-phenyl-1,2,4-dioxazolidine **6zz**. M.p. 68–69.5 °C (Found: C, 70.3; H, 6.8; N, 3.6. C₂₁H₂₄ClNO₂ requires C, 70.47; H, 6.77; N, 3.91%); δ_{H} (CCl₄) 0.7–2.0 (11 H, m), 2.11 (3 H, s, minor), 2.15 (3 H, s, major), 4.23 (1 H, br d, *J* 6) and 7.1–7.7 (9 H, m); δ_{C} (major isomer) 25.29, 25.80, 26.14, 28.35, 28.90, 37.79, 39.87, 102.37, 104.10, 127.70, 127.97, 128.12, 128.33, 129.10, 135.83, 138.37 and 141.69; δ_{C} (minor isomer) 25.26, 25.71, 26.07, 28.48, 28.83, 36.49, 39.29, 102.70, 103.19, 127.47, 127.99, 128.27, 128.57, 129.00, 134.02, 138.71 and 141.29.

Ozonolysis of the Vinyl Ether 1a in the Presence of a Mixture of Benzophenone 7a and the Imine 5b.—To a methylene dichloride solution (20 cm³) of the vinyl ether **1a** (200 mg, 2

mmol), benzophenone **7a** (364 mg, 2 mmol), and the imine **5b** (474 mg, 2 mmol), was passed a slow stream of ozone (2 mmol) at –70 °C. After evaporation of the solvent, the crude products were triturated with methanol to give the dioxazolidine **6b**. Column chromatography of the residue on silica gel (elution with benzene–hexane, 1:1) gave 3,3-diphenyl-1,2,4-trioxolane **9a** as oil; δ_{H} 5.37 (2 H, s) and 7.0–7.5 (10 H, m).²⁵

Competitive Reaction between Two Trapping Reagents.—To a mixture of a vinyl ether and two dipolarophiles in methylene dichloride or diethyl ether, was passed a stream of ozone at –70 °C. After evaporation of solvent, the ratio of the cycloadducts was determined by comparing the peak areas of the characteristic signals of each adduct in ¹H NMR spectra. **6b**: δ 4.99 (2 H, s); **6g**: δ 6.22 (1 H, s); **6l**: δ 5.45 (s) and 5.76 (s); **6m**: δ 5.58 (s) and 5.82 (s); **6zy**: δ 4.62 (2 H, s); **9a**: δ 5.37 (2 H, s);²⁶ **9b**: δ 6.33 (s) and 6.36 (s);^{2a} **9c**: δ 6.75 (1 H, br s);^{2a} **11**: δ 5.25 (2 H, s);⁴ **13a**: δ 6.65 (1 H, s);⁸ **13b**: δ 5.81 (1 H, s) and 6.69 (1 H, s).

Treatment of the Dioxazolidine 6h with Triethylamine.—A solution of compound **6h** (200 mg, 0.57 mmol) and triethylamine (58 mg, 0.57 mmol) in benzene (10 cm³) was stirred at room temp. for 24 h. After evaporation of the solvent, the mixture of crude products was triturated with hexane to give benzanilide **8**, which was recrystallized from ethyl acetate–hexane: m.p. 164–166 °C. The column chromatography of the residue on silica gel [elution with diethyl ether–benzene (1:9)] gave 4-*tert*-butylcyclohexanone **7c**: m.p. 47–50 °C.

Treatment of the Dioxazolidine 6d with Lithium Diisopropylamide.—To a tetrahydrofuran solution (20 cm³) of lithium diisopropylamide (2 mmol), was added a tetrahydrofuran solution (20 cm³) of compound **6d** (1 mmol) at 0 °C under nitrogen and the reaction was continued for a further 30 min at this temp. After work-up, the products were separated by column chromatography on silica gel. Elution with benzene gave benzophenone **7a** and subsequent elution with benzene–diethyl ether (1:1) gave compound **8**.

Treatment of Dioxazolidine 6d with Triphenylphosphine.—A solution of compound **6d** (100 mg) and triphenylphosphine (69 mg) in a NMR tube was kept at room temp. for 24 h. The ¹H NMR spectrum showed quantitative formation of benzophenone **7a** and *N*-phenylphenylmethanimine **5g**. After column chromatography on silica gel, eluting with benzene followed by diethyl ether–benzene (1:9) mixture, benzaldehyde **7e** (21 mg, 75%), benzophenone **7a** (48 mg, 100%) and aniline (22 mg, 90%) were isolated.

Thermolysis of Dioxazolidine 6d.—A frozen mixture of compound **6d** (100 mg) and benzene (2 cm³) in a glass tube was sealed under reduced pressure. Then the mixture was kept at 130 °C for 5 h. Subsequent column chromatography on silica gel (elution with benzene) gave first benzophenone **7a** and further elution with diethyl ether–benzene (1:9) gave compound **8**.

X-Ray Crystal Structure Determination of the Derivative Dioxazolidine 6d.*—A single crystal of compound **6d** (from ethyl acetate–hexane, approximate size 0.5 × 0.3 × 0.25 mm), mounted in a Lindemann tube, was used for X-ray data collection.

* The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Crystal data. $C_{26}H_{21}NO_2$, $M = 379.4$, colourless prisms, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.0750(16)$, $b = 10.5113(16)$, $c = 11.9132(22)$ Å, $\alpha = 71.184(13)$, $\beta = 86.895(17)$, $\gamma = 70.872(15)^\circ$, $U = 1014.6(8)$ Å³, $Z = 2$, D_c 1.242 g cm⁻³, $F(000)$ 400, $\mu(\text{Mo-K}\alpha) = 0.73$ cm⁻¹.

Data collection, structure solution and refinement. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer over the hemisphere (θ range: 1.0–25.0°; h : -9–+9, k : -11–+11, l : 0–+13) using Mo-K α X-radiation (λ 0.710 693 Å) and ω - 2θ scanning. Of the 2083 unique data measured, 1849 had $I > 2\sigma(I)$ and were used in subsequent structural solution and refinement. The data were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by direct methods (SHELXS86²⁷) and refined by full-matrix least squares methods (SHELX76²⁸) using anisotropic temperature factors for all the non-hydrogen atoms. All the hydrogen atoms were located on difference Fourier maps and included in the refinement process at idealised positions ($d_{\text{C-H}}$ 0.95 Å) with a fixed isotropic temperature factor (U_{iso} 0.10 Å²). At convergence, the discrepancy factors R and R_w were 0.040 and 0.042 respectively. The weighting scheme, $w^{-1} = [\sigma^2(F) + 0.000\ 183(F)^2]$ was found to give satisfactory analyses of variance. The final difference Fourier map was essentially featureless (general noise level less than ± 0.12 e Å⁻³). Incidental crystallographic calculations and compilation of tables were carried out using the computer program CALC.²⁹ Fig. 2 was prepared using the plotting program Ball & Stick.³⁰

Acknowledgements

We thank Dr. A. J. Welch, University of Edinburgh for access to X-ray data collection facilities and British Council (Tokyo) for the award of travel grants to K. J. McC. and M. N.

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Paper 4/04026K

Received 4th July 1994

Accepted 31st August 1994