Imines and Derivatives. Part 22.[1] Photoisomerization of the *N,N'*-Dioxides of *N,N'*-Dialkyl-2,2,4,4-tetramethylcyclobutane-1,3-di-imines

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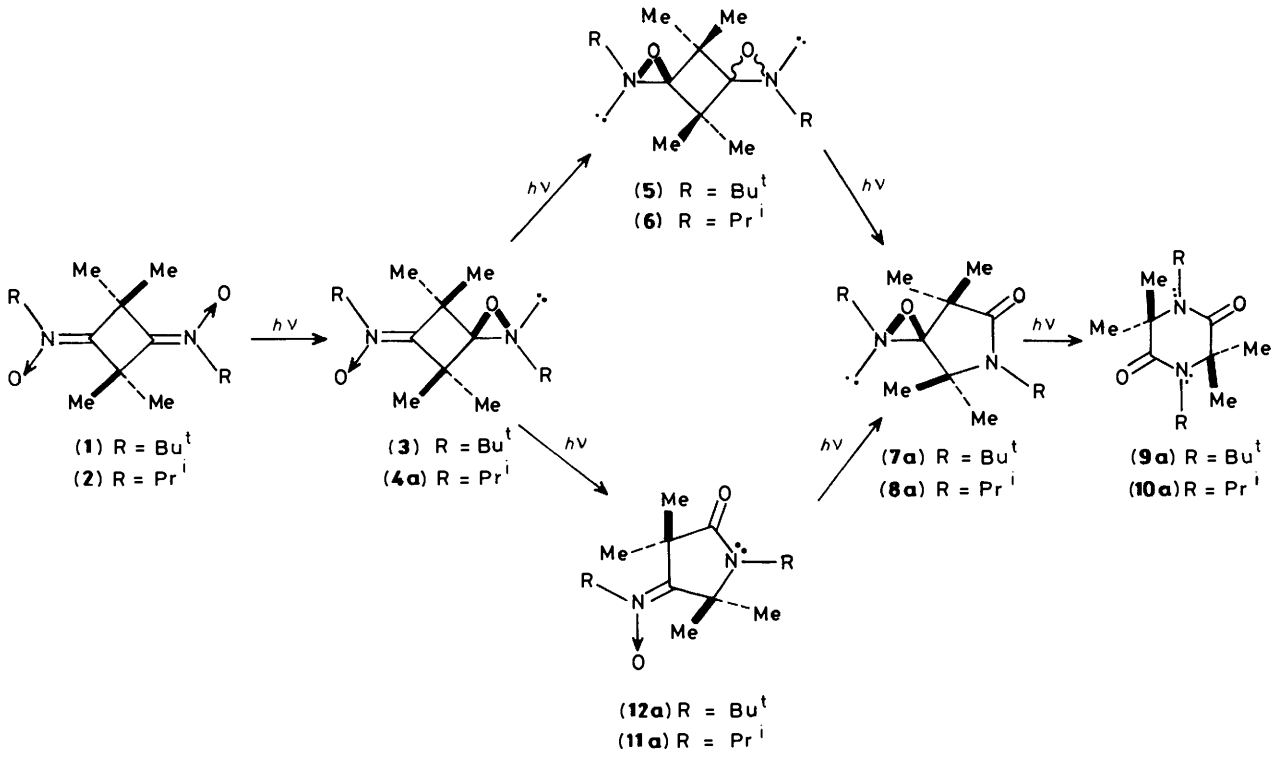
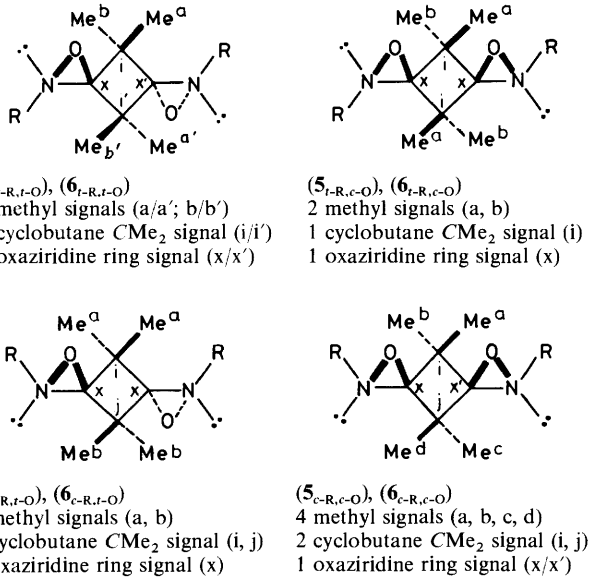
Photoisomerization of the *N,N'*-dioxides of two *N,N'*-dialkyl-2,2,4,4-tetramethylcyclobutane-1,3-di-imines occurs in a stepwise manner *via* the analogous mono-oxaziridine-mononitrone, dioxaziridine (and/or monoamide-mononitrone), and monoamide-mono-oxaziridine intermediates *en route* to the diamide products. The relative configurations of all products have been deduced by n.m.r. methods (chemical shift non-equivalence and n.O.e.d. spectroscopy). The stereochemistry of the photoisomerization reactions can be rationalized in terms of steric and stereoelectronic effects.

The photoisomerization reactions of imine *N*-oxides (nitrones) to yield isomeric amides was initially reported in the year 1910.[2] A period of almost 50 years elapsed, however, before the formation of oxaziridine intermediates during the photoisomerization of nitrones[3,4] could be confirmed experimentally.[5] The stereochemical relationship between the reactant nitrones and the initial oxaziridine products (and the configurational stability of each) in acyclic systems has previously been reported.[6–8] The present study (and the preliminary report[9]) is primarily concerned with a rationalization of the stereochemistry of both oxaziridine and amide photoisomerization products of the dinitrones (**1**) and (**2**) which were readily available from peroxyacid oxidation of the corresponding di-imines.[1,10]

Initial studies were carried out on the Bu^t substituted dinitrone (**1**), whose photoisomerization products were expected to be stabilized by the bulky *N*-Bu^t groups (Scheme 1). Thus, when the dinitrone (**1**) in dichloromethane solvent was irradiated using u.v. light (>300 nm), the oxaziridine products detected by ^{1}H n.m.r. analysis of the crude mixture were sufficiently stable to be separated by flash column chromatography (silica gel). The initial crystalline fractions to be eluted (*ca.* 52% yield) were identified as having the dioxaziridine structure (**5**) on the basis of their R_F values and spectral data and the ability of (**5**) to act as an oxygen-atom donor (and thus to generate iodine from an aqueous solution of hydrogen iodide). Only two dioxaziridine isomers could be detected by n.m.r. analysis of the dioxaziridine-containing chromatographic



Scheme 1. Photoisomerization products from dinitrones (**1**) and (**2**)



Scheme 2. Stereotopic relationships and predicted ^1H and ^{13}C n.m.r. signals for the four possible stereoisomers of the dioxaziridines (**5**) and (**6**). Different letters denote diastereotopic groups; primes denote enantiotopic groups

fractions from among the possible diastereoisomers: ($\mathbf{5}_{t\text{-R},t\text{-O}}$) (*trans*-R, *trans*-O), ($\mathbf{5}_{t\text{-R},c\text{-O}}$) (*trans*-R, *cis*-O), ($\mathbf{5}_{c\text{-R},t\text{-O}}$) (*cis*-R, *trans*-O), and ($\mathbf{5}_{c\text{-R},c\text{-O}}$) (*cis*-R, *cis*-O) (Scheme 2).

In principle, each of the four diastereoisomeric dioxaziridines (**5**) should be distinguishable by the presence (or absence) of homotopic/enantiotopic/diastereotopic ring methyl (^1H) or ring carbon atoms (^{13}C). In practice the ^1H and ^{13}C n.m.r. data for the two isolated dioxaridine diastereoisomers (**5**) can be assigned the ($\mathbf{5}_{t\text{-R},t\text{-O}}$) and ($\mathbf{5}_{t\text{-R},c\text{-O}}$) structures on the basis of a stereotopic analysis of the four possible isomers (Scheme 2). Thus the ^{13}C n.m.r. spectra of both isolated compounds showed only a single sharp signal for the cyclobutane ring CMe_2 and the oxaziridine ring carbon, together with two signals for the ring methyl groups. Unfortunately, neither an optically active solvent nor a chiral shift reagent can be used to distinguish between ($\mathbf{5}_{t\text{-R},t\text{-O}}$) and ($\mathbf{5}_{t\text{-R},c\text{-O}}$) structures since the latter isomer is chiral and the homotopic ring carbons therein could also give rise to double n.m.r. signals in a chiral medium (one set of signals for each enantiomer making the spectrum indistinguishable from achiral ($\mathbf{5}_{t\text{-R},t\text{-O}}$) which has internally enantiotopic ring carbons (Scheme 2).

Three observations suggest that the higher melting isomer of (**5**) (m.p. 131—134 °C) probably has the *trans*-R, *trans*-O configuration. This isomer moves faster on the silica-gel column, which is consistent with the absence of a net dipole moment in this isomer. The other isomers including *trans*-R, *cis*-O are polar. Secondly, the relatively small chemical-shift difference between the two ring methyl signals in the higher melting isomer ($\Delta\delta$ 0.06 and 0.7 p.p.m. in the ^1H and ^{13}C n.m.r. respectively) as compared with the lower melting isomer ($\Delta\delta$ 0.53 and 5.5 p.p.m.) is indicative of the former having the *trans*-R, *trans*-O configuration. The diastereotopic geminal ring methyl groups appear to be in a more markedly anisotropic environment in the *trans*-R, *cis*-O isomer, *i.e.* one of the geminal methyl groups is *syn* to both oxygen atoms and the other is *syn* to two nitrogen entities. Finally, the higher melting isomer showed fewer peaks than the low m.p. isomer in the range 600—1200 cm^{-1} in the i.r. spectrum, consistent with the former isomer having a centre of symmetry and thus having the *trans*-R, *trans*-O configuration.

No evidence for the presence of the alternative isomer

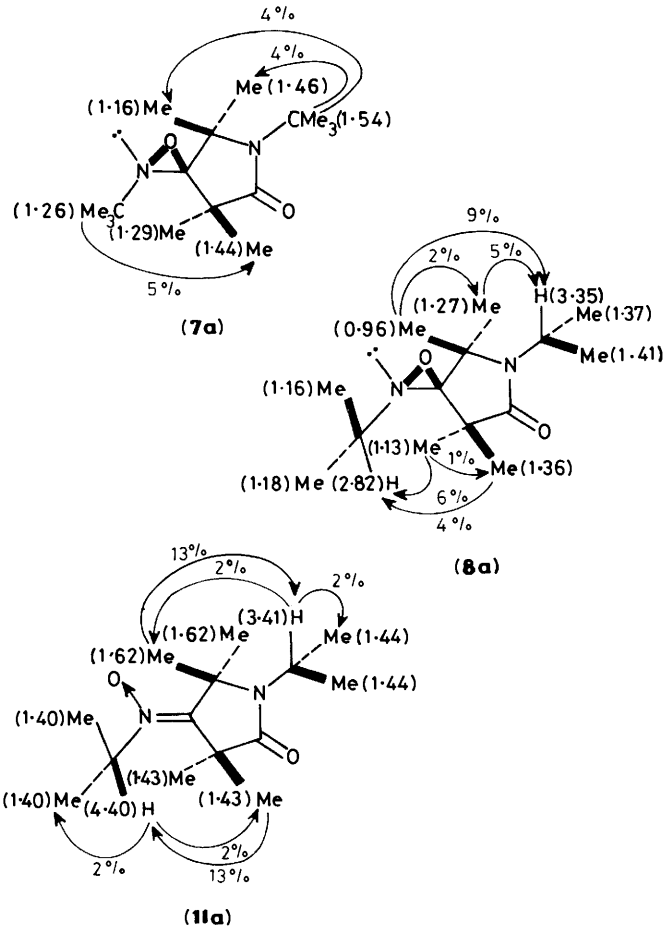
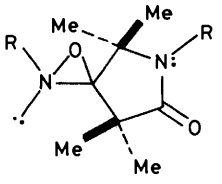


Figure 1. Intramolecular n.O.e. values (δ values) determined at 400 MHz in $CDCl_3$ solution

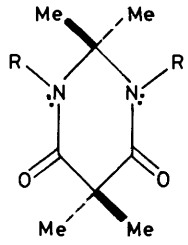
($\mathbf{5}_{c\text{-R},t\text{-O}}$) or ($\mathbf{5}_{c\text{-R},c\text{-O}}$) was evident in the n.m.r. spectra. The bias of isomers ($\mathbf{5}_{t\text{-R},t\text{-O}}$) (45%) and ($\mathbf{5}_{t\text{-R},c\text{-O}}$) (55%) is not considered to be significant in view of the possibility of a preferential photoisomerization of one dioxaziridine isomer to a monoamide-mono-oxaziridine (**7a,b**).



(**7b**; R = Bu^t)
(**8b**; R = Pr^i)

Further elution of the chromatography column loaded with the product mixture obtained from u.v. irradiation of dinitrone (**1**) yielded a second crystalline fraction (m.p. 94—96 °C, *ca.* 20% yield). This was identified as a monoamide-mono-oxaziridine on the basis of its oxidising power (hydrogen iodide), elemental microanalysis, and spectral data. The carbonyl absorption at 1 685 cm^{-1} in the i.r. spectrum was consistent with a γ-lactam ring. Structure (**7a**) was unequivocally established by n.O.e. difference spectroscopy (Figure 1). Irradiation of each *N*-t-butyl group gave n.O.e. enhancements on different sets of ring methyl groups thereby establishing that the structure was (**7a**) and not (**7b**).

Photoisomerization of the monoamide-mono-oxaziridine (**7a**) under similar photochemical conditions to those used for the dinitrone (**1**) was carried out. When the majority of the monoamide-mono-oxaziridine (**7a**) (*ca.* 90%) had been isomerized, the product mixture was separated by chromatography and a diamide product (**9a**) or (**9b**) was isolated. The



(**9b**; R = Bu^t)
(**10b**; R = Pr^i)

n.m.r. data for the diamide was only consistent with structure (**9a**) since a single sharp n.m.r. signal was observed for the ring methyl groups in both the ^{1}H and ^{13}C n.m.r. spectrum. The alternative diamide structure (**9b**) was not found among the other chromatography fractions. Thus, the total range of isolated and identified photoisomerization products obtained from dinitrone (**1**) included the dioxaziridines ($\mathbf{5}_{t\text{-R},t\text{-O}}$) and ($\mathbf{5}_{t\text{-R},c\text{-O}}$), the monoamide-mono-oxaziridine (**7a**) and the diamide (**9a**).

When the dinitrone (**2**) was irradiated under identical conditions with those used with the dinitrone (**1**), a wider range of photoisomerization products appeared to be present. The initially eluted fraction from a silica-gel column (pentane–ether, 85:15) was an isomeric mixture of dioxaziridines (**6**). This mixture was separated into two components by fractional crystallization of the appropriate chromatographic fractions and each was identified from the degree of non-equivalence of the ring methyl groups in the n.m.r. spectrum (Figure 2) as having the structures ($\mathbf{6}_{t\text{-R},t\text{-O}}$) and ($\mathbf{6}_{t\text{-R},c\text{-O}}$). As in the *N*-t-butyl analogues, the higher melting isomer (m.p. 150 °C), assigned the

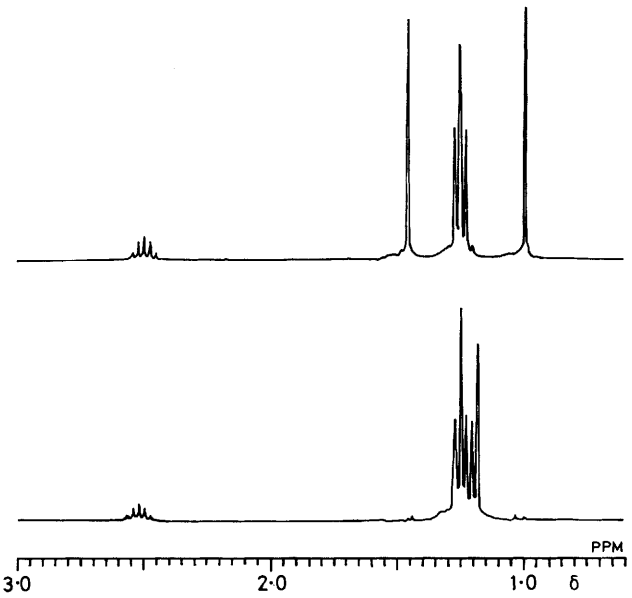
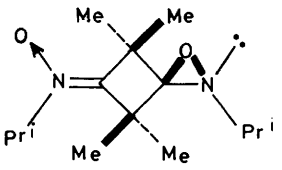


Figure 2. 270 MHz ^{1}H N.m.r. spectra of ($\mathbf{6}_{t\text{-R},t\text{-O}}$), (bottom) and ($\mathbf{6}_{t\text{-R},c\text{-O}}$), (top) recorded in deuteriochloroform

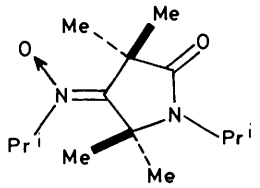
trans-R, *trans*-O structure, moves slightly faster on the column. A further crystalline fraction found to be eluted from the column (ether–methanol, 95:5) showed the spectral and chromatographic characteristics of a single mono-oxaziridine-mononitrone isomer. This compound was assumed to have structure (**4a**) rather than (**4b**) since both dinitrone (**2**) and the derived dioxaziridines ($\mathbf{6}_{t\text{-R},t\text{-O}}$) and ($\mathbf{6}_{t\text{-R},c\text{-O}}$) were found to have the Pr^i groups exclusively in a *trans*-relationship.

A monoamide-mono-oxaziridine product (**8a**) or (**8b**) was also isolated (pentane–ether, 1:1) as a photoisomerization product of the dinitrone (**2**). N.O.e. difference spectroscopy indicated that structure (**8a**) [rather than (**8b**)] had been formed exclusively (Figure 1).



(**4b**)

A further isolated photoproduct from the dinitrone (**2**) was identified as a monoamide-mononitrone (**11a**) or (**11b**). This product appears to have been derived from the mono-oxaziridine-mononitrone (**4a**). Structure (**11a**) was unequivocally assigned on the basis of n.O.e. difference spectroscopy



(**11b**)

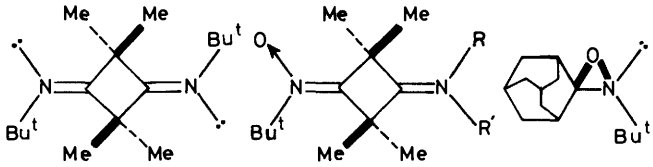
(Figure 1). Further u.v. irradiation of this monoamide-mononitrone isomer (**11a**) yielded both monoamide-mono-oxaziridine (**8a**) and diamide (**10a**) (Scheme 1). The latter product was also found after photoisomerization of the pure monoamide-mono-oxaziridine (**8a**). Structure (**10a**) rather than the isomeric structure (**10b**) was assigned on the basis of the ^{1}H n.m.r. spectrum. A summary of all the photoisomerization products derived from dinitrone (**2**) is shown in Scheme 1.

The presence of the mononitrone-mono-oxaziridine (**4a**), the dioxaziridine ($\mathbf{6}_{t\text{-R},c\text{-O}}$, $\mathbf{6}_{t\text{-R},t\text{-O}}$), the monoamide-mono-oxaziridine (**8a**), the monoamide-mononitrone (**11a**) and the diamide (**10a**) as products of photoisomerization of the dinitrone (**2**) suggests that the analogous derivatives of the dinitrone (**1**) should also result from u.v. irradiation. Unfortunately, neither the mononitrone-mono-oxaziridine (**3**) nor the monoamide-mononitrone (**12a**) could be detected among the photoproducts. This may be a result of (*a*) the presence of very small proportions of these isomers after the period of irradiation (which may be removed by recrystallization) and (*b*) the difficulties of detecting these compounds, (**3**) and (**12a**), by n.m.r. spectroscopy in comparison with the analogous derivatives (**4a**) and (**11a**) which showed a characteristic downfield septet due to the isopropyl group. It seems inconceivable that the dioxaziridines ($\mathbf{5}_{t\text{-R},t\text{-O}}$) and ($\mathbf{5}_{t\text{-R},c\text{-O}}$) could be formed by photoisomerization of the dinitrone (**1**) without proceeding *via* the mononitrone-mono-oxaziridine (**3**).

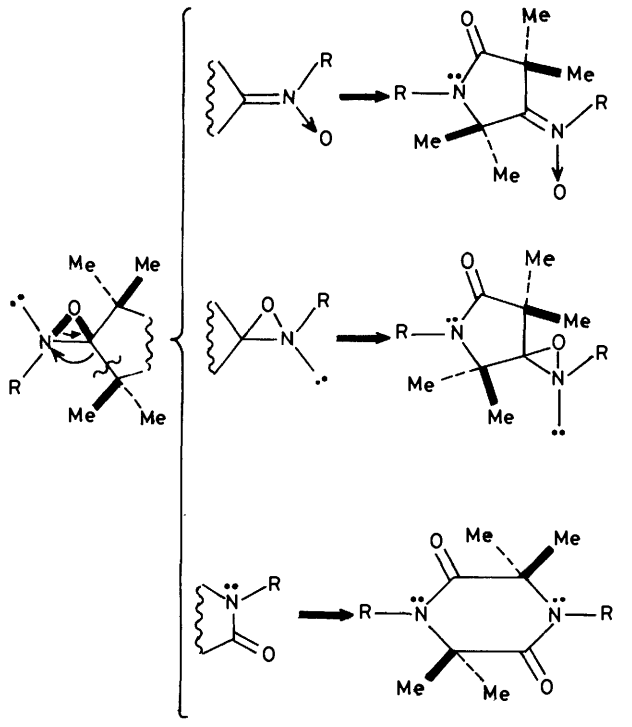
It is noteworthy that only half of the possible stereoisomeric products available from photoisomerization of the dinitrones (**1**) and (**2**) were in practice observed (Scheme 1). While these

were the only identifiable photoisomerization products, very minor proportions of other unidentified products were detected by ^{1}H n.m.r. analysis of crude product mixtures (before chromatography and recrystallization). A direct parallel between the stereochemistry of photoisomerization products of both the Bu^t and Pr^i series is evident and the stereochemical preference can be rationalized in terms of both steric and stereoelectronic effects.

The exclusive formation of the *trans*-dinitrones (**1**) and (**2**) results from steric interactions between the R-groups and proximate gem-dimethyl substituents on the cyclobutane ring. Recent *X*-ray crystallographic studies[1] on the di-imine (**13**) and the mononitrone-mono-oxime isomers (**14a,b**) indicate the presence of severe non-bonding interactions between *N*-Bu^t and neighbouring geminal dimethyl groups on the cyclobutane ring. This effect is evident from the marked bond angle distortions observed.[1] A similar effect is likely to be present in the mononitrone-mono-oxaziridine (**3**) or dioxaziridine products ($\mathbf{5}_{t\text{-R},t\text{-O}}$) and ($\mathbf{5}_{t\text{-R},c\text{-O}}$) from u.v. irradiation of the dinitrione (**1**). In view of the relatively low inversion barriers found for the spiro-oxaziridine (**15**)[11] ($\Delta G^{\ddagger}$ 25 kcal mol^{-1}) it is possible that the increased steric effects present in the dioxaziridines ($\mathbf{5}_{t\text{-R},t\text{-O}}$, $\mathbf{5}_{t\text{-R},c\text{-O}}$) will result in spontaneous inversion at the pyramidal N atoms at ambient temperature (configurational instability). The observed preference for the *trans*-configuration in dioxaziridines ($\mathbf{5}_{t\text{-R},t\text{-O}}$) and ($\mathbf{5}_{t\text{-R},c\text{-O}}$) may thus be the equilibrium distribution resulting from steric interactions. Similar, although smaller steric effects are expected in the *N*-isopropyl dioxaziridines ($\mathbf{6}_{t\text{-R},t\text{-O}}$, $\mathbf{6}_{t\text{-R},c\text{-O}}$), though these ought to be configurationally stable by analogy with other *N*-Pr^i substituted oxaziridines[11] ($\Delta G^{\ddagger}$ > 30 kcal mol^{-1}).



(**13**) (**14a**) R = OH, R′ = lone pair (**15**)
(**14b**) R′ = OH, R = lone pair



Scheme 3.

The stereochemical configurations of both monoamide and diamide photoproducts may be directly correlated with specific oxaziridine stereoisomers. In all cases, cleavage of the carbon–carbon bond *anti* to the nitrogen lone pair occurs exclusively (Scheme 3).

These results are in total accord with the stereoelectronic theory proposed by Deslongchamps[12] where two heteroatoms and a leaving group are linked to a common carbon atom. This theory has been supported by recent theoretical studies[13] and the experimental results of Lattes *et al.*[14] who have also found that stereoelectronic control can occur during photoisomerization of mono-oxaziridines to monoamides. The present studies have been extended to show that stereoelectronic control can also be found in the thermal isomerization of oxaziridines to amides. Thus, when the dioxaziridine ($\mathbf{5}_{t\text{-R},t\text{-O}}$, $\mathbf{5}_{t\text{-R},c\text{-O}}$) was heated in 1,2,4-trichlorobenzene (*ca.* 110 °C), the monoamide mono-oxaziridine (**7a**) was formed almost exclusively. Similarly, heating the latter product at a higher temperature (*ca.* 160 °C) in the same solvent gave only the diamide isomer (**9a**).

Experimental

N.m.r. spectra were recorded using 90 MHz (Bruker WH-90), 250 MHz (Bruker WM-250) and 400 MHz (Bruker WH-400) instruments. Unless stated otherwise the ^{1}H spectra were obtained in $CDCl_3$ solution using tetramethylsilane as reference. ^{13}C N.m.r. spectra were determined at 22.63 MHz (Bruker WH-90) or 62.8 MHz (Bruker WM-250). N.O.e. difference spectra were obtained using the 400 MHz instrument. Mass spectral data was obtained using an AEI MS902 (updated by V.G. Instruments Ltd.) mass spectrometer. Photoisomerizations were carried out using a medium pressure Hg lamp (500 W) from a Hanovia Reading Reactor (> 300 nm). The sample was irradiated in a Pyrex vessel (solution path length < 10 mm) which was maintained at ambient temperature by use of a water-cooled inner jacket and an electric fan.

The synthesis of 2,2,4,4-tetramethyl-*N*,*N*′-di-t-butylcyclobutane-1,3-di-imine *N*,*N*′-dioxide (**1**) and *N*,*N*′-di-isopropyl-2,2,4,4-tetramethylcyclobutane-1,3-di-imine *N*,*N*′-dioxide (**2**) has been reported previously.[1] A typical photoisomerization procedure for the dinitrones (**1**) and (**2**) was carried out as follows. A solution of the dinitrone (**1**) (20 mmol) in dichloromethane (100 ml) in a Pyrex tube equipped with a water-cooled inner jacket was stirred magnetically under an atmosphere of nitrogen at ambient temperature whilst being irradiated with a u.v. lamp. Aliquots were periodically removed and analysed by n.m.r. and t.l.c. until starting material was shown to have disappeared (16 h). The solvent was then removed under reduced pressure and the concentrated residues were subjected to flash column chromatography on silica-gel (Merck Kieselgel 60, column size 21 × 7 cm). Elution with pentane–diethyl ether (85:15) yielded a mixture of the following dioxaziridines (**5**) which were partially separated by chromatography and further purified by crystallization from pentane: 4,4,8,8-*tetramethyl*-trans-2,7-*di-t-butyl*-trans-1,6-*dioxa*-2,7-*diazadispiro*[2.1.2.1]-*octane* ($\mathbf{5}_{t\text{-R},t\text{-O}}$) (32%), m.p. 131—134 °C (pentane) (Found: C, 68.15; H, 11.0; N, 10.0. $C_{16}H_{30}N_2O_2$ requires C, 68.0, H, 10.7; N, 9.9%); δ_H(250 MHz; $CDCl_3$) 1.18 (6 H, s, 2 × Me^a), 1.19 (18 H, s, 2 × Bu^t), and 1.24 (6 H, s, 2 × Me^b); δ_C(62.81 MHz; $CDCl_3$) 21.1 (CMe_2), 21.8 (CMe_2), 26.9 (2 × CMe_3), 49.8 (2 × CMe_2), 57.6 (2 × CMe_3), and 92.6 (OCN).

4,4,8,8-*Tetramethyl*-trans-2,7-*di-t-butyl*-cis-1,6-*dioxa*-2,7-*diazadispiro* [2.1.2.1]*octane* ($\mathbf{5}_{t\text{-R},c\text{-O}}$) (23%), m.p. 90—93 °C

(pentane) (Found: C, 68.0; H, 10.9, N, 9.9. $C_{16}H_{30}N_2O_2$ requires C, 68.0; H, 10.7; N, 9.9%); δ_H(250 MHz; $CDCl_3$) 0.96 (6 H, s, 2 × Me[a]), 1.19 (18 H, s, 2 × Bu[t]), and 1.49 (6 H, s, 2 × Me[b]); δ_C(62.81 MHz; $CDCl_3$) 17.9 (CMe_2), 23.4 (CMe_2), 26.9 (2 × CMe_3), 49.8 (2 × CMe_2), 57.6 (2 × CMe_3), and 92.7 (OCN).

Further elution from the chromatography column using pentane–diethyl ether (1:1) gave the monoamide-mono-oxaziridine 4,4,7,7-*tetramethyl*-trans-2,5-*di-t-butyl*-1-*oxa*-2,5-*diazaspiro*[2.4]*heptan*-6-*one* (**7a**) (20%), m.p. 94—96 °C (aq. methanol) (Found: C, 68.1; H, 10.6; N, 9.9. $C_{16}H_{30}N_2O_2$ requires C, 68.0; H, 10.7; N, 9.9%); δ_H(400 MHz; $CDCl_3$) 1.16 (3 H, s, Me), 1.26 (9 H, s, Bu[t]), 1.29 (3 H, s, Me), 1.44 (3 H, s, Me), 1.46 (3 H, s, Me), and 1.54 (9 H, s, Bu[t]).

Elution of the chromatography column using diethyl ether–methanol (95:5) after prolonged irradiation of the dinitrone (**1**) or monoamide-mono-oxaziridine (**7a**) gave variable yields of 3,3,6,6-*tetramethyl-di-t-butylpiperazine*-2,5-*dione* (**9a**), m.p. 161—162 °C (methanol) (Found: C, 68.0; H, 10.9; N, 9.9. $C_{16}H_{30}N_2O_2$ requires C, 68.0; H, 10.7; N, 9.9%); δ_H(250 MHz; $CDCl_3$) 1.57 (18 H, s, 2 × Bu[t]) and 1.68 (12 H, s, 4 × Me); δ_C(67.8 Mz, $CDCl_3$) 29.1 (2 × CMe_2), 30.4 (2 × CMe_3), 59.8 (2 × CMe_3), 65.3 (2 × CMe_2), and 173.4 (2 × C=O).

Photolysis of the dinitrone (**2**) under the previously specified conditions was carried out and the reaction was terminated after 18 h. The dichloromethane extract was concentrated and the pentane-soluble component chromatographed on silica gel. Elution with pentane–ether (95:5) yielded a mixture of the following dioxaziridines ($\mathbf{6}_{t\text{-}R,t\text{-}O}$, $\mathbf{6}_{t\text{-}R,c\text{-}O}$) which were separated by fractional recrystallization from pentane: trans-2,7-*di-isopropyl*-4,4,8,8-*tetramethyl*-trans-1,6-*dioxa*-2,7-*diazadispiro*-[2.1.2.1]*octane* ($\mathbf{6}_{t\text{-}R,t\text{-}O}$) (21%), m.p. 150 °C (pentane) (Found: C, 65.8; H, 10.0; N, 10.9. $C_{14}H_{26}N_2O_2$ requires C, 66.1; H, 10.0; N, 11.0%); δ_H(270 MHz; $CDCl_3$) 1.18 (6 H, s, CMe_2), 1.21 (6 H, d, *J* 6.2 Hz, CHMe_2), 1.24 (6 H, s, CMe_2), 1.26 (6 H, d, *J* 6.2 Hz, CHMe_2), and 2.51 (2 H, sept, *J* 6.2 Hz, 2 × CHMe$_2$); δ_C(62.81 MHz; $CDCl_3$) 21.1 (CMe_2), 21.8 (CMe_2), 27.0 (2 × CHMe_2), 49.8 (2 × CMe_2), 57.6 (2 × CHMe$_2$), and 92.7 (OCN); trans-2,7-*di-isopropyl*-4,4,8,8-*tetramethyl*-cis-1,6-*dioxa*-2,7-*diazadi-spiro*[2.1.2.1]*octane* ($\mathbf{6}_{t\text{-}R,c\text{-}O}$) (21%), m.p. 121—123 °C (pentane) (Found: C, 66.2; H, 10.1; N, 11.3. $C_{14}H_{26}N_2O_2$ requires C, 66.1; H, 10.0; N, 11.0%); δ_H(270 MHz, $CDCl_3$) 0.99 (6 H, s, CMe_2), 1.23 (6 H, d, *J* 6.0 Hz, CHMe_2), 1.26 (6 H, d, *J* 6.0 Hz, CHMe_2), 1.45 (6 H, s, CMe_2), and 2.49 (2 H, sept, *J* 6.2 Hz, 2 × CHMe_2); δ_C(62.81 MHz, $CDCl_3$) 17.9 (CMe_2), 23.4 (CMe_2), 26.9 (2 × CHMe_2), 49.9 (2 × CMe_2), 57.6 (2 × CHMe$_2$).

The monoamide-mono-oxaziridine (**8a**) was eluted using pentane–diethyl ether (1:1) to give: trans-2,5-*di-isopropyl*-4,4,7,7-*tetramethyl*-1-*oxa*-2,5-*diazaspiro*[2.4]*heptan*-6-*one* (**8a**) (24%), m.p. 94—96 °C (aq. methanol) (Found: C, 66.1; H, 10.0; N, 11.3. $C_{13}H_{26}N_2O_2$ requires C, 66.1; H, 10.2; N, 11.0%); δ_H(250 MHz; $CDCl_3$) 1.01 (3 H, s, Me), 1.19 (3 H, s, Me), 1.20 (3 H, d, *J* 6.3 Hz, CHMe_2), 1.24 (3 H, d, *J* 6.3 Hz, CHMe_2), 1.32 (3 H, s, Me), 1.42 (3 H, d, *J* 6.6 Hz, CHMe_2), 1.46 (3 H, d, *J* 6.6 Hz, CHMe$_2$), 2.88 (1 H, sept, *J* 6.3 Hz, CHMe$_2$), and 3.39 (1 H, sept, *J* 6.6 Hz, CHMe$_2$).

The mononitrone-mono-oxaziridine (**4**) was eluted using diethylether–methanol (95:5) to give trans-N-(2-*isopropyl*-4,4,6,6-*tetramethyl*-1-*oxa*-2-*azaspiro*[2.3]*hexan*-5-*ylidene*)-*propylamine* N-*oxide* (**4a**) (24%), m.p. 88—90 °C (pentane) (Found: C, 66.0; H, 10.3; N, 11.0. $C_{14}H_{26}N_2O_2$ requires C, 66.1; H, 10.2; N, 11.0%); δ(250 MHz, C_6D_6), 1.01 (3 H, d, *J* 6.2 Hz, CHMe_2), 1.06 (3 H, s, Me), 1.18 (3 H, s, Me), 1.26 (3 H, d, *J* 6.2 Hz, Me), 1.29 (3 H, d, *J* 6.6 Hz, CHMe_2), 1.32 (3 H, d, *J* 6.6 Hz, Me), 1.66 (3 H, s, Me), 1.70 (3 H, s, Me), 2.35 (1 H, sept, *J* 6.2 Hz, CHMe$_2$), and 3.66 (1 H, sept, *J* 6.6 Hz, CHMe$_2$).

The pentane-insoluble component of the product mixture obtained from u.v. irradiation of the dinitrone (**2**), when subjected to column chromatography (silica gel) gave with dichloromethane–methanol (95:5) as eluant the pure monoamide mononitrone (**11a**). The latter compound was obtained in *ca.* 12% yield after recrystallization from dichloromethane–pentane. In common with many nitrones, decomposition occurred upon melting (indefinite m.p.) as olefin elimination occurred. The material finally solidified as the mono-oxime product of high m.p. (> 250 °C).

1-*Isopropyl*-4-*isopropylimino*-3,3,5,5-*tetramethylpyrrolidin*-2-*one* N^4-*oxide* (**11a**) (12%), m.p. 165—180 °C (decomp.) (Found: C, 66.2; H, 10.2; N, 11.1. $C_{13}H_{26}N_2O_2$ requires C, 66.1; H, 10.3; N, 11.0); δ_H(400 MHz; $CDCl_3$) 1.40 (6 H, d, *J* 6.4 Hz, CHMe_2), 1.43 (6 H, s, Me), 1.44 (6 H, d, *J* 6.8 Hz, CHMe_2), 1.62 (6 H, s, Me), 3.41 (1 H, d, *J* 6.8 Hz, CHMe$_2$), and 4.40 (1 H, d, *J* 6.4 Hz, CHMe$_2$). Traces of diamide product (**10a**) were detected after photorearrangement of the dinitrone (**2**). A pure sample of the diamide (**10a**) was, however, obtained by complete photoisomerization of the monoamide-mononitrone (**11a**) [*via* the monoamide-mono-oxaziridine after a lengthy period of irradiation (45 h)].

1,4-*Di-isopropyl*-3,3,6,6-*tetramethylpiperazine*-2,5-*dione* (**10a**), m.p. 181—184 °C (benzene–pentane) (Found: C, 66.2; H, 10.2; N, 11.1. $C_{14}H_{26}N_2O_2$ requires C, 66.1; H, 10.3; N, 11.0%); δ_H(400 MHz; $CDCl_3$) 1.42 (6 H, d, *J* 6.8, CHMe_2), 1.48 (6 H, s, Me), and 3.46 (2 H, sept, *J* 6.8, CHMe$_2$).

Acknowledgements

We thank the S.E.R.C for financial support (to N. D. S.), and for providing an allocation of time on the Regional 400 MHz n.m.r. service at Warwick.

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Received 27*th June* 1988; *Paper* 8/02523A