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STERIC AND STEREOELECTRONIC EFFECTS IN THE SYNTHESIS AND PHOTOISOMERIZATION OF A DINITRONE OF 2,2,4,4-TETRAMETHYLCYCLOBUTANEDIONE[1]

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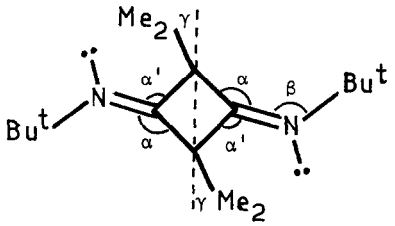
Abstract: Peroxyacid oxidation of diimine (1) yielded only the trans isomer of dinitrone (2) which upon photoisomerization gave dioxaziridines (3a) and (3b) and amide (4) as the only isolable isomers; an X-ray crystallographic investigation of (1) shows a considerable geometry distortion.

The synthesis of diimine (1) has been reported previously.[2] The exclusive formation of the trans isomer, previously deduced from n.m.r. analysis, has now been confirmed by an X-ray crystal structure analysis.[3] The cyclobutane ring is planar as found in the parent diketone[4] and derivatives,[4,5] and the imino nitrogens and the t-butyl quaternary carbons lie in the ring plane. Steric interactions between the t-butyl groups and the ring CMe_2 substituents in diimine (1) result in a marked geometry distortion.



$\alpha = 144.0^\circ$
$\alpha' = 122.6^\circ$
$\beta = 127.9^\circ$
$\gamma = 6.2^\circ$
[γ is the dihedral angle between the CMe_2 plane and the vertical plane through C(2) and C(4)].

Figure

The distorted bond angles are given in the Figure. The exocyclic CCN bond angles α and α' in (1) differ by over 20°, the Bu^tNC angle β is enlarged to 127.9°, and the CMe_2 groups are displaced out of the vertical plane and away from the nearest t-butyl group. The instability of the cis isomer can be rationalized since an analogous local cyclobutane geometry would suffer a buttressing interaction between the CMe_2 group and the flanking t-butyl groups.

Oxidation of diimine (1) using m-chloroperoxybenzoic acid in dichloromethane or chloroform gave dinitrone (2), m.p. 106°, in 55% yield. The trans configuration was assigned on the basis of the equivalence of the ring methyl groups in the 250 MHz ^1H n.m.r. spectrum:

δ_H ($CDCl_3$) 1.56 (18H, s, $2Bu^t$) and 1.76 (12H, s, 4Me). The reaction may be under thermodynamic control as the barrier to cis-trans isomerization in nitrones is lowered under acidic conditions,[6] and the exclusive formation of the trans-isomer can be explained by buttressing effects. Dioxaziridines (3a) or (3b) were not formed by direct peroxyacid oxidation of diimine (1).

Exposure of dinitrone (2) to u.v. radiation (λ > 300 nm, medium pressure Hg lamp) at ambient temperature afforded the novel dispiro oxaziridines (3a) and (3b) together with other products. Short column chromatography on silica-gel followed by recrystallization gave (3a), 32%, m.p. 131-134°; δ_H ($CDCl_3$) 1.18 (6H, s, 2Me), 1.19 (18H, s, $2Bu^t$), 1.24 (6H, s, 2Me); δ_C ($CDCl_3$) 21.1 (2Me), 21.8 (2Me), 26.9 ($2Me_3$), 49.8 ($2CMe_2$), 57.6 ($2CMe_3$), 92.6 (2CO); and isomer (3b), 23%, m.p. 90-93°; δ_H ($CDCl_3$) 0.96 (6H, s, 2Me), 1.19 (18H, s, $2Bu^t$), 1.49 (6H, s, 2Me); δ_C ($CDCl_3$) 17.9 (2Me), 23.4 (2Me), 26.9 ($2Me_3$), 49.8 ($2CMe_2$), 57.6 ($2CMe_3$), 92.7 (2C-O). The quaternary carbon signal at δ 92.6 is characteristic of an oxaziridine ring, and both compounds liberated iodine from acidified iodide. The equivalence of the two sets of CMe_2 groups in the ^1H and ^{13}C n.m.r. spectra excludes isomers (3c) and (3d) which possess cis N-Bu^t groups.[7] Both dioxaziridines (3a) and (3b) were found to be remarkably stable at ambient temperature.

Another product, 20%, m.p. 94-96° was also eluted from the column and identified as the amide-oxaziridine (4) on the basis of infrared and n.m.r. data: ν_{CO} 1685 cm^{-1}; δ_H ($CDCl_3$) 1.16 (3H, s, Me), 1.26 (9H, s, Bu^t), 1.28 (3H, s, Me), 1.44 (3H, s, Me), 1.46 (3H, s, Me), and 1.54 (9H, s, Bu^t). The configuration (4), rather than (6), was established by intramolecular n.O.e. difference spectra on a degassed solution at 400 MHz. Selective irradiation of the amide Bu^t signal (δ 1.54) gave ca. 4% enhancements on the adjacent CMe_2 signals at δ 1.16 and 1.46, and irradiation of the oxaziridine Bu^t signal (δ 1.26) gave ca. 5% enhancement on a different ring methyl signal (δ 1.44).

Further irradiation of either dioxaziridines (3a) and (3b) or amide-oxaziridine (4) yielded a diamide, m.p. 161-162°, which was eluted with ether-methanol (95:5) from silica gel and identified as 1,4-di-t-butyl-3,3,6,6-tetramethylpiperazine-2,5-dione (5): ν_{CO} 1650 cm^{-1}; δ_H ($CDCl_3$) 1.57 (18H, s, $2Bu^t$) and 1.68 (12H, s, 4Me). No evidence was found for the formation of the isomeric diamide (7), which would show two sets of ring methyl signals in the n.m.r. spectrum (all four ring methyl signals in (5) are isochronous).

The structure and stereochemistry of the products obtained in the photo-induced ring expansions (3)→(4)→(5) are consistent with stereoelectronic control,[8] i.e. the C-C bond cleavage occurs anti to the oxaziridino nitrogen lone pair.[9] This is in accord with a recently proposed theory and example of stereoelectronic control in the photo-isomerization of oxaziridines to amides.[10] The ring expansion can also be achieved thermally, thus oxaziridine (3) rearranges at ca. 110° in 1,2,4-trichlorobenzene solution mainly to the amide (4). On further heating at ca. 160°, (4) yields the diamide (5) as the major product. The formation of diamide (5) by a thermally or photochemically induced double ring expansion of dioxaziridines (3a) and (3b) represents a novel synthetic approach to the piperazine dione ring system.

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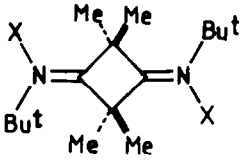
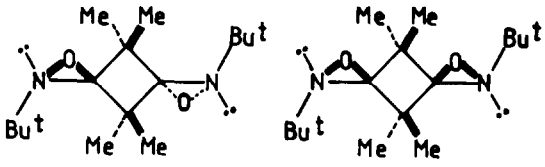
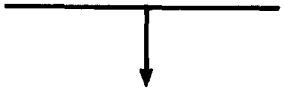


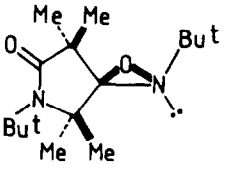


(3a) (3b)

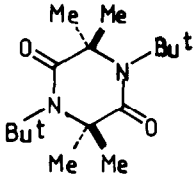
(1) X = lone pair

(2) X = O

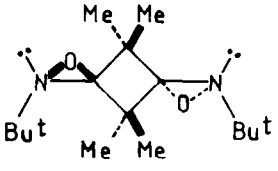




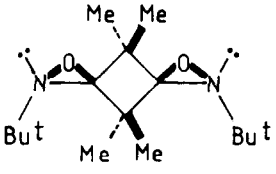
(4)



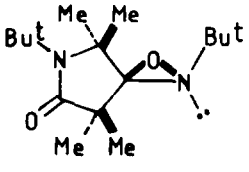
(5)



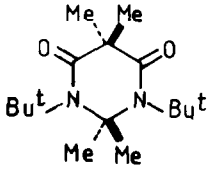
(3c)



(3d)



(6)



(7)

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1. Supplementary data are available for diimine (1) [atomic fractional coordinates, temperature factors, molecular dimensions, and structural factors]. See Announcement to Authors, Tetrahedron Lett., 1983, 5154, and ref. 3.

2. J. Bjorgo, D.R. Boyd, W.B. Jennings, P.M. Muckett and L.C. Waring, J. Org. Chem., 1977, 42, 3700.

3. Crystal data for (1): $C_{16}H_{30}N_2$, M = 250.4, monoclinic, space group $P2_1/n$, a = 8.201(8), b = 17.486(18), c = 6.201(6) Å, β = 107.0°, U = 883.9 Å^3, Z = 2, Mo-K_α radiation λ = 0.71069 Å. Data were measured on a Stoe STADI-2 diffractometer to 2θ = 60°. The structure was solved by direct methods using 879 independent reflections and was refined by least squares to a final R = 8.7%, allowing anisotropic vibrations for C and N atoms and with inclusion of isotropic H atoms, located in a difference Fourier synthesis. The molecule lies on a crystallographic centre of symmetry. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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7. The configurational distinction between the two NBu^t trans isomers (3a) and (3b) is tentative and was inferred from their spectra. Thus, the isomer with the greater chemical shift difference between the geminal ring methyl groups in the ^1H and ^{13}C n.m.r. spectrum was assigned to (3b) where the oxygen atoms are cis. The geminal methyls are also diastereotopic in (3a) but the difference in the magnetic environment is expected to be much smaller as each methyl is cis to one oxygen. Isomer (3a) also appears to have fewer absorptions in the infrared spectrum than (3b), consistent with the presence of a centre of symmetry in (3a).

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9. N-Alkyloxaziridines are normally configurationally stable at ambient temperature, though bulky substituents can lower the nitrogen inversion barrier, see J. Bjorgo and D.R. Boyd, J.C.S. Perkin Trans. II, 1973, 1575.

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