Imines and Derivatives. Part 21.[1] A Study of Structural and Mechanistic Aspects of the Synthesis of Imine, Imine Oxide, and Oxime Derivatives of 2,2,4,4-Tetramethylcyclobutane-1,3-Dione by *X*-Ray Crystallography and Nuclear Magnetic Resonance and Ultraviolet Spectroscopy

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The dinitrone derivatives (**5a, b**) of 2,2,4,4-tetramethylcyclobutane-1,3-dione were synthesised by peroxyacid oxidation of the corresponding di-imines (**3a, b**). *X*-Ray crystallographic analysis of di-imine (**3a**) and the hydroxyimino nitrone isomers (**6a, b**) indicate a marked buttressing effect leading to an exclusive preference for the *trans* geometry in di-imine (**3a**) and dinitrone (**5a**). Thermal elimination reactions of the *N*-Bu^t substituted nitrones (**5a**), (**6a**), and (**8a**) to yield oximes and 2-methylpropene have been investigated by u.v. kinetic studies. The results are consistent with a concerted mechanism involving a five-membered cyclic transition state.

The synthesis of di-imines (**3a, b**) from 2,2,4,4-tetramethylcyclobutane-1,3-dione has been reported in a previous study of the mechanism of *E–Z* isomerization in trialkyl imines.[2] The observed total preference for the *E*-configuration of di-imine (**3a**) at equilibrium in solution was attributed *a priori* to a buttressing effect between the *gem* dimethyl groups and the proximate *N*-alkyl groups. A similar effect was also assumed[3] to account for the exclusive formation of the *E*-isomer of the dinitrone (**5a**) derived from a direct oxidation of di-imine (**3a**). The present *X*-ray crystallography study was undertaken in order to obtain definitive evidence of the buttressing effects in di-imine (**3a**) and dinitrone (**5a**).

Low-temperature recrystallization of di-imine (**3a**) from pentane yielded large, well formed, plate-like crystals which showed some deterioration in the air but, when sealed in capillary tubes, were suitable for *X*-ray crystallographic analysis. The preliminary form of the present study[4] reported several of the distorted dihedral angles and bond angles of di-imine (**3a**). Atomic co-ordinates are given in Table 1 and bond lengths and angles in Table 2. A projection of the molecule is shown in Figure 1.

The molecule lies on a crystallographic centre of symmetry and the central cyclobutane ring is necessarily planar. The planarity extends to the imine nitrogens, N(1,1′), and the central carbons, C(5,5′), of the Bu^t groups (maximum deviation of any atom from the mean plane through eight atoms is 0.02 Å). The internal angles vary according to the state of hybridization of the carbon atom (θ_1, sp^2: 93.4°; θ_2, sp^3: 86.6°; Figure 2). Earlier *X*-ray structures of cyclobutane ring systems similar to di-imine (**3a**), *i.e.* diketone (**1**)[5] and di-imine (**10**)[6] were also found to contain a planar diamond-shaped cyclobutane ring.

A particularly noteworthy feature of the structure of di-imine (**3a**) was the marked degree of distortion of the exocyclic bond angles ($\varphi_1 = 144.0°$; $\varphi_2 = 122.6°$; $\alpha = 127.9°$) and of the *gem* dimethyl groups which are displaced out of the vertical plane and away from the nearest Bu^t group, as indicated by the angle between the bisector of the Me–C–Me angle and the C(2)–C(2′) line ($\Omega = 6.2°$). The decreased degree of distortion observed for comparable bonds in di-imine (**10**) ($\varphi_1 = 137.4°$; $\varphi_2 = 128.6°$; $\alpha = 119.5°$; $\Omega = 4.4°$), which had not previously been commented upon,[6] was due to the smaller steric requirements of the 4-bromophenyl group compared with the bulky t-butyl group in di-imine (**3a**). On the basis of the *X*-ray data for both di-imines (**3a**) and (**10**) it is now clear that the larger buttressing effect between the *N*-Bu^t and *gem* dimethyl groups in di-imine (**3a**) can account for the absence of the *Z*-isomer of (**3a**) at equilibrium. The smaller buttressing effect in di-imine (**10**) is reflected in the lower degree of bond angle distortion and in the higher proportion of *Z*-isomer (33%) of the comparable di-imine (**11**) found at equilibrium in solution.[7]

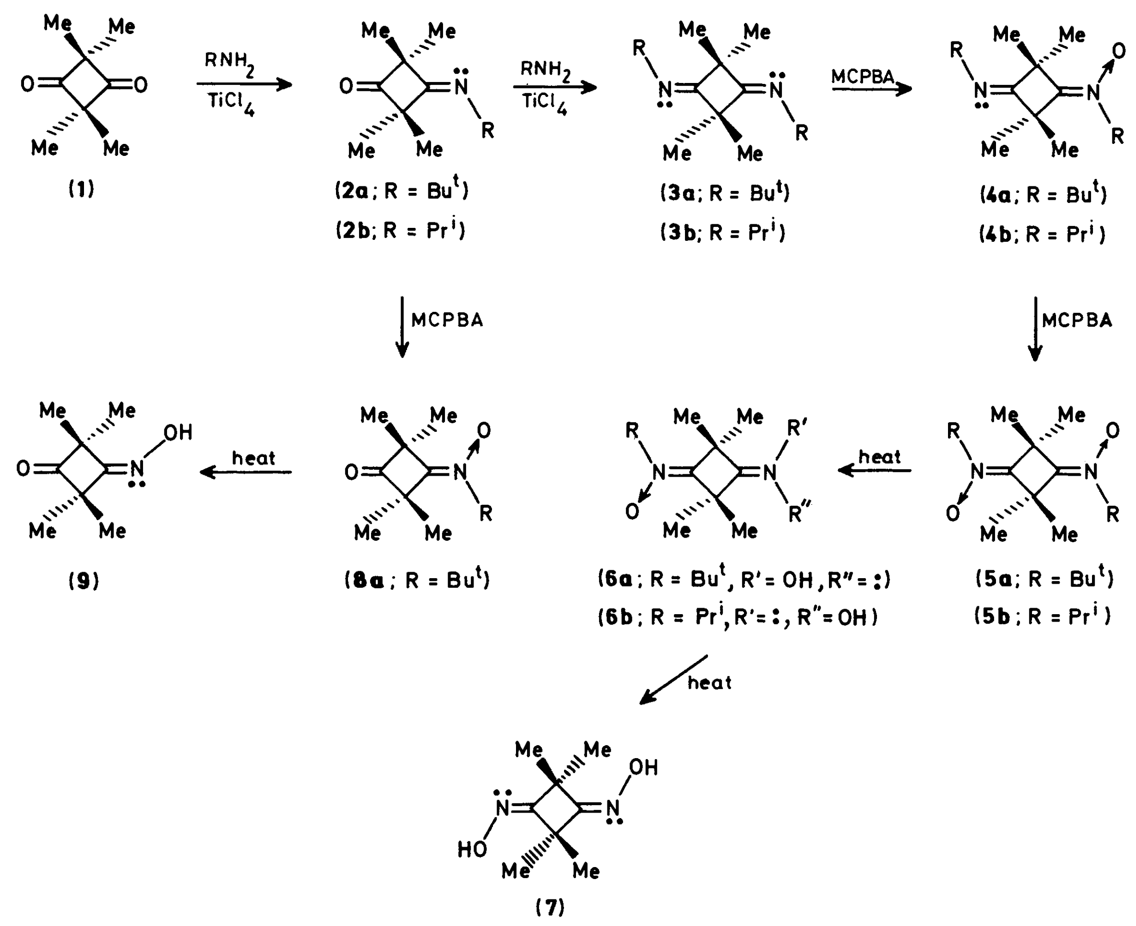
Table 1. Atomic fractional co-ordinates for compound (**3a**)

Atom	*x*	*y*	*z*
N(1)	0.074 9(5)	0.122 3(2)	0.125 7(5)
C(1)	0.045 2(5)	0.053 6(2)	0.069 0(6)
C(2)	0.122 0(5)	−0.027 6(2)	0.098 2(6)
C(3)	0.274 4(6)	−0.040 8(3)	0.010 2(8)
C(4)	0.147 1(6)	−0.066 2(3)	0.330 6(7)
C(5)	0.232 3(5)	0.155 1(2)	0.277 2(7)
C(6)	0.336 7(9)	0.185 0(5)	0.125 0(11)
C(7)	0.173 2(8)	0.222 9(3)	0.392 9(11)
C(8)	0.334 5(8)	0.102 7(3)	0.462 0(10)

Table 2. Bond lengths and angles in compound (**3a**)

Atoms	Length	Atoms	Angle (°)
N(1)–C(1)	1.254(5)	C(2)–C(1)–C(2′)	93.4(5)
N(1)–C(5)	1.473(5)	C(2)–C(1)–N(1)	144.0(3)
C(1)–C(2)	1.542(5)	C(2′)–C(1)–N(1)	122.6(3)
C(1)–C(2′)	1.527(5)	C(1)–C(2)–C(3)	116.6(3)
C(2)–C(3)	1.521(7)	C(1)–C(2)–C(4)	116.7(3)
C(2)–C(4)	1.549(6)	C(1′)–C(2)–C(3)	112.3(3)
C(5)–C(6)	1.540(10)	C(1′)–C(2)–C(4)	110.5(3)
C(5)–C(7)	1.536(8)	C(3)–C(2)–C(4)	111.6(3)
C(5)–C(8)	1.515(7)	C(1)–N(1)–C(5)	127.9(3)
		N(1)–C(5)–C(6)	106.4(4)
		N(1)–C(5)–C(7)	105.2(4)
		N(1)–C(5)–C(8)	115.8(3)
		C(6)–C(5)–C(7)	109.4(5)
		C(7)–C(5)–C(8)	107.1(4)
		C(6)–C(5)–C(8)	112.6(4)

The increased proportion of the *Z*-isomer of di-imine (**3b**) (21%) in equilibrium with the *E*-isomer (**3b**) (79%), as found by



Scheme.

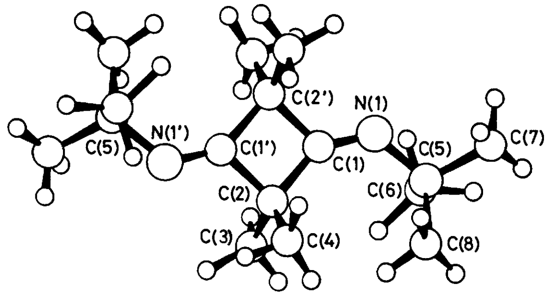
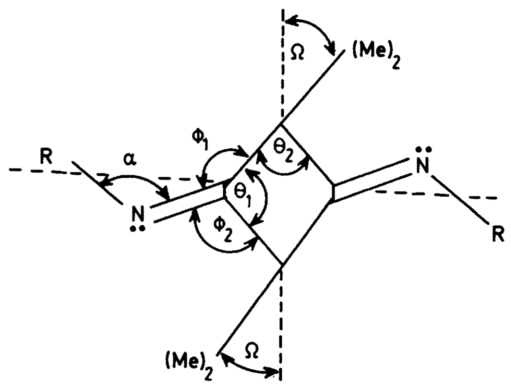


Figure 1. Atom numbering scheme of di-imine (**3a**)



R
(**3a**) Bu^t
(**10**) 4-BrC$_6$H$_4$
(**11**) Ph

Figure 2.

n.m.r. analysis of the sample in CDCl$_3$ solution, is clearly also a result of the reduced buttressing effects. The intermediate imino ketone compounds (**2a**, **b**) assumed to be formed during the synthesis of di-imines (**3a**,**b**) were not generally isolated since an excess of amine was used. When a reduced quantity of t-butylamine relative to dione (**1**) was used however the anticipated imino ketone (**2a**) was obtained.

m-Chloroperoxybenzoic (MCPBA) acid oxidation of di-imines (**3a**) and (**3b**) in dichloromethane solution gave dinitrones (**5a**) and (**5b**), respectively in approximately 50% yield after column chromatographic purification. Evidence of the isomeric mono- or di-oxaziridine isomers was not obtained. The dioxaziridine isomers (obtained by an alternative route[4]) were found to be stable during the oxidation and work-up conditions used and could not thus have spontaneously decomposed. The formation of dinitrones (**5a**,**b**), and the absence of the corresponding dioxaziridines, may be largely accounted for by the steric effects of the *gem* dimethyl groups which hinder the approach of the peroxyacid from the preferred orthogonal direction required during oxaziridine formation.

The stereochemistry of both di-imine (**3a**), (*E*, 100%)[2] and (**3b**), (*E*, 79%: *Z*, 21%)[2] and the resultant dinitrone products (**5a**, **b**), (*E*, 100%) was also determined by both ^{1}H and ^{13}C n.m.r. spectroscopy. The exclusive formation of the *E*-isomer of

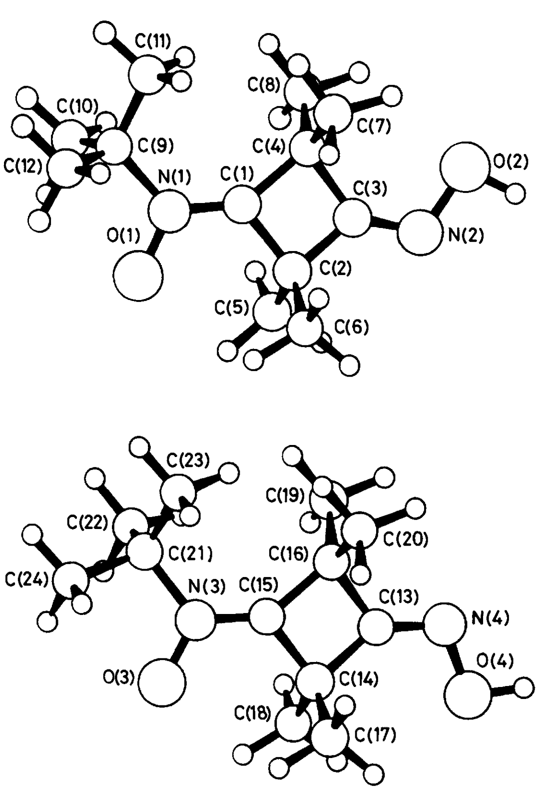
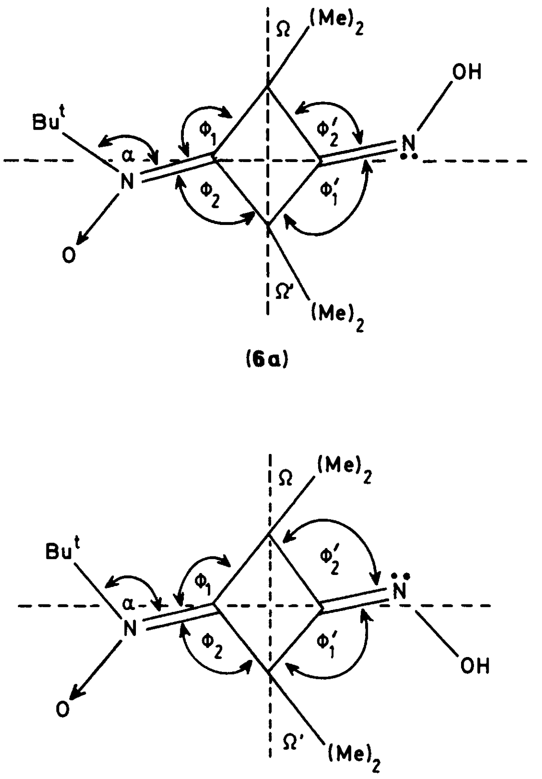


Figure 3. (a) Atom numbering scheme of hydroxyimino nitrone (**6a**) (*E*); (b) hydroxyimino nitrone (**6b**) (*Z*)

Table 3. Atomic fractional co-ordinates for compound (**6**)

Atom	*x*	*y*	*z*
C(1)	0.343 6(4)	0.205 2(4)	0.676 2(8)
C(2)	0.417 4(4)	0.201 0(4)	0.829 2(8)
C(3)	0.498 6(4)	0.209 4(4)	0.704 8(10)
C(4)	0.428 3(4)	0.218 7(5)	0.548 7(10)
C(5)	0.418 3(5)	0.099 6(5)	0.919 5(10)
C(6)	0.412 6(5)	0.290 8(5)	0.959 8(9)
C(7)	0.436 1(5)	0.323 3(6)	0.471 7(11)
C(8)	0.444 7(6)	0.133 3(6)	0.419 1(11)
C(9)	0.167 0(5)	0.191 5(4)	0.545 0(9)
C(10)	0.135 0(9)	0.085 3(7)	0.525 6(15)
C(11)	0.203 5(8)	0.222 4(11)	0.382 2(15)
C(12)	0.082 8(7)	0.257 1(9)	0.593 9(14)
N(1)	0.246 0(3)	0.195 3(3)	0.690 1(7)
N(2)	0.594 6(4)	0.206 7(4)	0.739 7(8)
O(1)	0.207 6(3)	0.181 6(3)	0.839 9(6)
O(2)	0.650 8(3)	0.214 2(4)	0.591 7(8)
C(13)	0.195 9(4)	0.516 7(4)	0.946 8(9)
C(14)	0.189 2(4)	0.568 7(4)	1.118 9(8)
C(15)	0.195 8(4)	0.666 3(4)	1.020 5(8)
C(16)	0.211 6(4)	0.612 3(4)	0.848 4(8)
C(17)	0.279 4(5)	0.546 3(4)	1.241 4(9)
C(18)	0.089 2(4)	0.552 3(4)	1.206 7(10)
C(19)	0.132 9(5)	0.625 4(5)	0.702 0(9)
C(20)	0.319 7(4)	0.617 5(5)	0.778 1(10)
C(21)	0.171 6(5)	0.853 8(4)	0.984 2(10)
C(22)	0.060 4(5)	0.856 9(5)	0.921 1(11)
C(23)	0.246 9(5)	0.857 5(5)	0.844 0(12)
C(24)	0.190 1(6)	0.942 5(4)	1.113 6(11)
N(3)	0.181 5(3)	0.755 1(3)	1.086 7(7)
N(4)	0.190 9(3)	0.427 4(3)	0.882 2(7)
O(3)	0.168 7(3)	0.765 4(3)	1.250 5(6)
O(4)	0.171 9(3)	0.355 9(3)	1.009 1(6)



(6a)

(6b)

Figure 4.

dinitrones (**5a**) and (**5b**) by peroxyacid oxidation of the corresponding di-imines (**3a**) and (**3b**) may again largely result from the buttressing effects between *gem* dimethyl groups and *N*-alkyl substituents. The *E*-isomers of dinitrones (**5a**) and (**5b**) were found to decompose upon heating without any evidence of the *Z* forms being obtained. This observation, allied to the previous report[8] that the barrier to *E–Z* isomerization of nitrones is markedly reduced in the presence of acid catalysts, suggests that no *Z*-isomer of dinitrones (**5a**) and (**5b**) is present at equilibrium. Comparable *X*-ray crystallographic evidence of the buttressing effect in di-imine (**3a**) was thus sought for dinitrone (**5a**).

Several attempts to obtain a suitable crystal of dinitrone (**5a**) by recrystallization were unsuccessful. Using the most satisfactory solvent system (benzene–pentane) and a slow recrystallization procedure generally yielded a conglomerate of poorly formed crystals. One of these recrystallized samples which had been allowed to stand at ambient temperature over several weeks was however found to contain a tiny proportion of well formed elongated square prismatic crystals growing round the sides of the vessel and protruding from the surface of the main crop. The prominent crystals which were selected for *X*-ray crystallographic analysis subsequently proved to be a mixture of *Z*- and *E*-isomers of the hydroxyimino nitrone (**6a, b**) with one molecule of each isomer in the asymmetric unit. The very small quantity of these prominent crystals presumably arose from a minor degree of partial thermal decomposition of dinitrone (**5a**) after recrystallization. The distribution of crystals of hydroxyimino nitrone isomers (**6a, b**) in the vial was consistent with their formation by sublimation.

Projections of the two isomers (**6a, b**) are shown in Figures 3(a) and (b). The atomic co-ordinates are listed in Table 3 and bond lengths and bond angles in Table 4. The central cyclobutane rings are not quite planar, exhibiting folds of 3.5° (**6a**) and 6.7° (**6b**) across the line of the carbons which carry the *gem* dimethyl groups.

Table 4. Bond lengths and angles in (**6**)

(a) Bond lengths

Atoms	Length (Å)	Atoms	Length (Å)
C(1)–C(2)	1.529(7)	C(13)–C(14)	1.509(8)
C(2)–C(3)	1.470(9)	C(14)–C(15)	1.516(8)
C(3)–C(4)	1.524(9)	C(15)–C(16)	1.534(8)
C(1)–C(4)	1.529(9)	C(13)–C(16)	1.508(8)
C(2)–C(5)	1.525(8)	C(14)–C(17)	1.543(7)
C(2)–C(6)	1.556(8)	C(14)–C(18)	1.519(8)
C(4)–C(7)	1.521(9)	C(16)–C(19)	1.541(7)
C(4)–C(8)	1.524(10)	C(16)–C(20)	1.542(8)
C(1)–N(1)	1.301(7)	C(13)–N(4)	1.277(6)
C(3)–N(2)	1.291(7)	C(15)–N(3)	1.290(7)
N(2)–O(2)	1.397(8)	N(4)–O(4)	1.409(7)
N(1)–O(1)	1.305(6)	N(3)–O(3)	1.305(6)
N(1)–C(9)	1.524(7)	N(3)–C(21)	1.547(8)
C(9)–C(10)	1.468(9)	C(21)–C(22)	1.537(8)
C(9)–C(11)	1.440(13)	C(21)–C(23)	1.500(11)
C(9)–C(12)	1.465(10)	C(21)–C(24)	1.552(9)

(b) Angles

Atoms	Angle (°)	Atoms	Angle (°)
C(1)–C(2)–C(3)	86.3(5)	C(13)–C(14)–C(15)	85.3(5)
C(2)–C(3)–C(4)	95.9(4)	C(14)–C(15)–C(16)	94.1(4)
C(3)–C(4)–C(1)	84.5(5)	C(15)–C(16)–C(13)	84.7(5)
C(4)–C(1)–C(2)	93.3(4)	C(16)–C(13)–C(14)	95.5(4)
N(1)–C(1)–C(2)	122.8(6)	N(4)–C(13)–C(14)	139.1(6)
N(1)–C(1)–C(4)	143.9(6)	N(4)–C(13)–C(16)	125.4(6)
N(2)–C(3)–C(2)	125.6(6)	N(3)–C(15)–C(14)	124.0(6)
N(2)–C(3)–C(4)	138.5(7)	N(3)–C(15)–C(16)	141.6(6)
C(3)–N(2)–O(2)	111.0(6)	C(13)–N(4)–O(4)	110.7(5)
C(1)–N(1)–O(1)	119.8(5)	C(21)–N(3)–O(3)	115.1(5)
C(1)–N(1)–C(9)	126.8(6)	C(15)–N(3)–O(3)	120.0(5)
O(1)–N(1)–C(9)	113.3(5)	C(15)–N(3)–C(21)	124.8(6)
C(1)–C(2)–C(6)	116.3(5)	C(13)–C(14)–C(17)	113.9(5)
C(1)–C(2)–C(5)	114.0(4)	C(13)–C(14)–C(18)	114.2(4)
C(5)–C(2)–C(3)	112.7(5)	C(15)–C(14)–C(17)	116.0(4)
C(6)–C(2)–C(3)	114.5(5)	C(15)–C(14)–C(18)	114.8(4)
C(5)–C(2)–C(6)	111.1(6)	C(17)–C(14)–C(18)	110.6(5)
C(1)–C(4)–C(7)	115.6(5)	C(13)–C(16)–C(19)	112.9(4)
C(1)–C(4)–C(8)	117.4(6)	C(13)–C(16)–C(20)	111.3(5)
C(3)–C(4)–C(8)	111.9(5)	C(15)–C(16)–C(19)	119.6(5)
C(3)–C(4)–C(7)	111.1(5)	C(15)–C(16)–C(20)	116.0(5)
C(7)–C(4)–C(8)	113.0(7)	C(19)–C(16)–C(20)	109.9(6)
N(1)–C(9)–C(10)	106.6(5)	N(3)–C(21)–C(22)	105.4(5)
N(1)–C(9)–C(11)	114.7(6)	N(3)–C(21)–C(23)	111.6(5)
N(1)–C(9)–C(12)	107.6(6)	N(3)–C(21)–C(24)	106.5(6)
C(10)–C(9)–C(11)	107.0(9)	C(22)–C(21)–C(23)	114.0(6)
C(10)–C(9)–C(12)	111.7(8)	C(22)–C(21)–C(24)	108.6(6)
C(11)–C(9)–C(12)	109.2(8)	C(23)–C(21)–C(24)	110.5(6)

Enlargement of the bond angle, α, from idealized trigonal geometry in the hydroxyimino nitrone isomers (**6a**; 126.8°; **6b**; 124.8°, Figure 4) was comparable to that found in the di-imine (**3a**; $\alpha = 127.9°$). Similarly the bond angle distortion in compounds (**6a**) and (**6b**), indicated by the values for $\varphi_1 - \varphi_2$ (21.1 and 17.6°, respectively), are comparable with the values found in di-imine (**3a**; $\varphi_1 - \varphi_2 = 21.4°$). The displacements from the vertical planes of the *gem* dimethyl groups away from the Bu^t groups in (**6a**) and (**6b**) are comparable with di-imine (**3a**); (**6a**; Ω 6.2°; **6b**; $\Omega = 6.7°$). These observations suggest that similar types of buttressing effects between the *N*-Bu^t group and the *gem* dimethyl groups exist in di-imine (**3a**), in the nitrone portion of the hydroxyimino nitrone isomers (**6a, b**), and thus presumably also in the dinitrone (**5a**). Conversely the diminished degree of bond angle distortion associated with the oxime portion of the hydroxyimino nitrone isomers (**6a**; $\varphi_1' - \varphi_2' = 12.9°$; **6b**; $\varphi_1' - \varphi_2' = 13.7°$) reflects the decreased buttressing effect found with the smaller hydroxy groups. The displacement of the *gem* dimethyls away from the nitrone oxygen atom is also decreased both with respect to the lone pair (**6a**; $\Omega' = 1.8°$) and to the hydroxy group (**6b**; $\Omega' = 1.6°$).

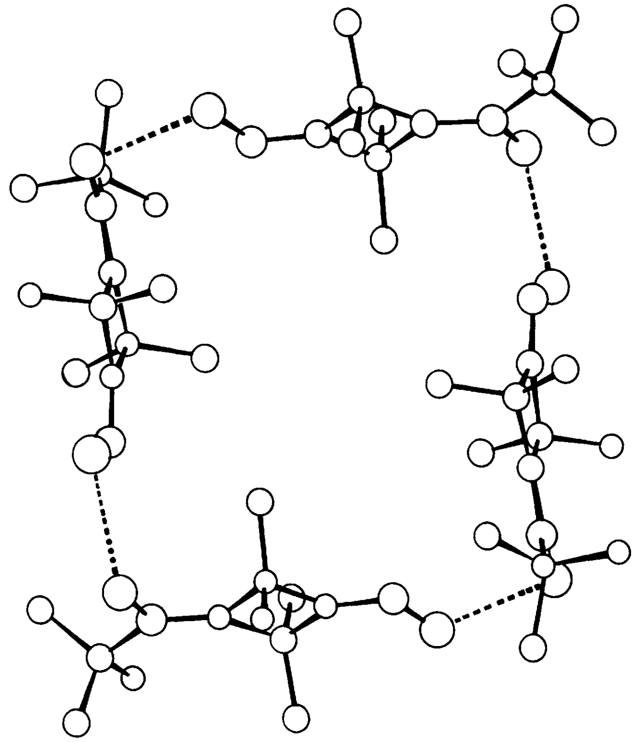


Figure 5. Four-molecule cluster containing two molecules each of (**6a**) and (**6b**). (For clarity hydrogen atoms are omitted)

A further point of structural interest is the formation, through intermolecular hydrogen-bonding between oxime and nitrone oxygen atoms, of cyclic clusters comprising two molecules each of isomers (**6a**) and (**6b**) per cluster. Although the hydrogen atoms of the oximes were not located in the structure analysis the intermolecular O(oxime) • • • O(nitrone) distances, 2.67 and 2.68 Å, and the four independent N–O • • • O angles are consistent with a structure in which each oxime hydrogen is hydrogen bonded to the nitrone oxygen of an adjacent molecule. This ring formation is illustrated in Figure 5. There is one such ring per unit cell. It is likely therefore that the co-crystallization of the two isomers is a consequence of this packing efficiency.

The unexpected presence of a very small proportion of the hydroxyimino nitrone isomers (**6a, b**) as partial thermal decomposition products in a sample of the dinitrone (**5a**) initiated a more detailed study of this elimination reaction. Previous studies[8,9] on the thermal elimination reaction of diaryl keto nitrones to form oximes and olefins indicated a superficial similarity with the thermal elimination reaction of teriary amine oxides (Cope elimination). Prior to the present study the thermal elimination reaction had not been observed for dialkyl keto nitrones.

A preliminary examination of the thermal decomposition of dinitrone (**5a**) in the solid state indicated that melting occurred at *ca.* 106 °C. The resulting liquid evolved a gas at *ca.* 120 °C before solidifying to form a crystalline sample of dioxime (**7**) which melted at 280—281 °C. On a preparative scale, the *E*-dioxime (**7**) was isolated in quantitative yield after heating a solid sample of dinitrone (**5a**) in a sealed tube. The 2-methylpropene generated was liquified by cooling (−196 °C) and characterized by mass spectrometry.

The hydroxyimino nitrone intermediate (**6**) could not be

Table 5. Rate constants for the thermal elimination reactions of dinitrone (**5a**)

T (°C)	61	65	70	75	76	79	80
$10^5k_1/\mathrm{s}^{-1}$	1.8	3.3	4.8	8.0	9.9	12.1	15.9[b]
k_1/k_2	—	—	3.2	2.4	2.3[c]	2.6	3.2[c]

[a] In 2,2,4-trimethylpentane solvent. [b] Using butanol solvent, $k_1 = 7.5 \times 10^{-5}\ \mathrm{s}^{-1}$, $k_1/k_2 = 3.9$. [c] k_1/k_2 calculated from values of k_2 using the hydroxyimino nitrone (**6a**) as reactant are 2.2 (76 °C) and 1.9 (80 °C).

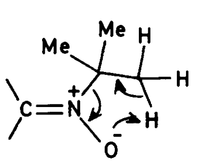


Figure 6.

isolated from heating dinitrone (**5a**) in the solid state but was observed as a short-lived intermediate during n.m.r. analysis of a heated (*ca.* 120 °C) sample of (**5a**) in $C_6D_5CD_3$ solvent. When a preparative-scale sample of dinitrone (**5a**) was heated in toluene solution at 110 °C for 5 min, crystallization of the hydroxyimino nitrone (**6**) from solution occurred. On the basis of ^1H and ^{13}C n.m.r. spectral data this hydroxyimino nitrone product (**6**) appeared to be present as a single isomer. In view of (a) the *E* stereochemistry of the dinitrone reactant (**5a**), (b) the exclusive formation of the *E*-isomer of dioxime (**7**) from heating either this sample of hydroxyimino nitrone (**6**) or dinitrone (**5a**) and (c) the different crystal characteristics of this sample of hydroxyimino nitrone (**6**) from that which yielded the crystal structure in Figure 5, compound (**6**) is assumed to have the *E* configuration.

A kinetic study of the thermal elimination of the dinitrone (**5a**), hydroxyimino nitrone (**6a**), and the keto nitrone (**8a**) in solution was carried out in a thermostatically controlled cell using u.v. spectroscopy. The nitrone chromophore in compounds (**5a**), (**6a**), and (**8a**) was found to have a maximum absorption ($\lambda_{\max.}$) at 272 nm although the extinction coefficient ($\varepsilon_{\max.}$) of dinitrone (**5a**) was approximately four-fold larger than that of the hydroxyimino nitrone (**6a**). Using the peak at 272 nm as a monitor of reaction progress in the sequence (**5a**) $\xrightarrow{k_1}$ (**6a**) $\xrightarrow{k_2}$ (**7**), the absorbance (A) is given by equation (1), where ε_1, ε_2, and ε_3 are the absorption coefficients for compounds (**5a**),

$$A = \varepsilon_1 C_1 + \varepsilon_2 C_2 + \varepsilon_3 C_3 \qquad (1)$$

(**6a**), and (**7**) present at concentrations C_1, C_2, and C_3, respectively. The solutions of the differential equations for a system of two consecutive reactions are well known[10] and C_1, C_2, and C_3 may be expressed in terms of C_0, the initial concentration of (**5a**) and the rate constants k_1 and k_2. The variation of absorbance with time was then fitted to equation (1), using equations (2)—(4) to calculate C_1, C_2, and C_3, by

$$C_1 = C_0 \exp(-k_1 t) \qquad (2)$$

$$C_2 = C_0 k_1 [\exp(-k_1 t) - \exp(-k_2 t)]/(k_2 - k_1) \qquad (3)$$

$$C_3 = C_0 - C_1 - C_2 \qquad (4)$$

adjusting the values of the rate constants. The constant k_1 dominated the first 100 min of a 600 min kinetic run at 80 °C while k_2 dominated the final 300 min. At the lower temperatures only k_1 could be measured since the half-life of the second stage had risen to *ca.* 20 h which was beyond the time-scale of the experiments. The rate constants k_1 and k_2 are given in Table 5.

Experiments were also performed with the hydroxyimino nitrone (**6a**) to obtain the rate constant k_2 directly. The fitting technique enabled the measurement of k_1 with considerably greater accuracy than k_2 so that the directly measured values of k_1/k_2 are the more reliable. The mean value of k_1/k_2, 2.7 ± 0.4 found by the former method was not significantly different from the value of 2.1 suggested by the direct method and both are in agreement with the statistically calculated value of 2.

The thermal elimination of 2-methylpropene from the structurally similar ketonitrone (**8a**) during formation of the keto oxime (**9**) was studied in 2,2,4-trimethylpentane at 80 °C. The rate constant k_3 ($3.3 \times 10^{-5}\ \mathrm{s}^{-1}$) was found to be less than that found for thermal decomposition of the hydroxyimino nitrone (**6a**), k_2 ($8.4 \times 10^{-5}\ \mathrm{s}^{-1}$). Although this is unexpected on any electronic or steric grounds, the molecular charge distribution and solvation may be very different for the two molecules.

The enthalpy of activation for the *N*-Bu^t nitrone eliminations of compound (**5a**) and (**6a**) is apparently insensitive both to solvent and to the structure of the remainder of the molecule. The data in Table 5 yield a value of $\Delta H^\ddagger = 101 \pm 5.0\ \mathrm{kJ\ mol^{-1}}$ which is comparable with the value of $107.8 \pm 1.6\ \mathrm{kJ\ mol^{-1}}$ found in both t-butyl alcohol and decahydronaphthalene for *N*-(fluoren-9-ylidene)-t-butylamine *N*-oxide in which there is a structurally similar nitrone group.[9] Although these activation energies are not significantly different, some changes in rate can occur as the solvent is varied. The acceleration produced by non-hydroxylic solvents which was noted previously[9] seems to be more marked for the hydroxyimino nitrone (**6a**) than for the dinitrone (**5a**). The statistically expected value of k_1/k_2 is only observed in 2,2,4-trimethylpentane suggesting that solvation effects destabilize the transition state for the elimination process in hydroxylic solvents.

Previous kinetic studies on the thermal elimination of diaryl *N*-Bu^t nitrones[9] suggest that the reaction proceeds *via* a non-synchronous concerted mechanism involving a highly ordered cyclic transition state with N–C bond cleavage considerably in advance of O–H bond formation.

The present kinetic studies on nitrones (**5a**), (**6a**), and (**8**) are consistent with a similar mechanism and transition state. While the conformations adopted by the hydroxyimino nitrone isomers (**6a**, **b**) in the crystal lead to distances of 2.33 and 2.37 Å, between the nitrone oxygen atom and the closest hydrogen atom of the Bu^t group, free rotation about single bonds in solution, without any change in bond lengths or angles, would yield a closest approach of 1.82 and 1.86 Å, respectively. These distances, which are readily attainable in a planar cyclic O–N–C–C–H transition state, could clearly facilitate a concerted *syn* elimination mechanism (Figure 6).

Experimental

Crystal Data for (**3a**).—$C_{16}H_{30}N_2$, $M = 250.4$. Monoclinic, $a = 8.201(8)$, $b = 17.486(18)$, $c = 6.201(6)$ Å, $\beta = 107.0(1)°$, $V = 850.2$ Å^3, space group $P2_1/n$ (alt. $P2_1/c$, No. 14), $Z = 2$, $D_x = 0.98\ \mathrm{g\ cm^{-3}}$, $F(000) = 280$, $\lambda = 0.710\,69$ Å, colourless plates, $\mu(\text{Mo-}K_\alpha) = 0.62\ \mathrm{cm^{-1}}$.

Data Collection, Analysis, and Refinement.—Stöe STADI2 diffractometer, graphite-monochromated Mo-K_α radiation, ω-scan mode, scan width 1.0°, scan speed 1.0 deg min^{-1}; 879 unique reflections measured ($2.5 \leqslant \theta \leqslant 30°$). Direct methods (MULTAN[11]). Least-squares refinement, non-hydrogen atoms anisotropic. Hydrogen atoms located in difference Fourier, refined with individual isotropic temperature factors. Final $R = 0.087$.[12]

Crystal Data for (**6**).*—$C_{12}H_{22}N_2O_2$, $M = 226.3$. Triclinic, $a = 13.190(13)$, $b = 13.204(13)$, $c = 7.840(8)$ Å, $\alpha = 90.9(1)$, $\beta = 91.4(1)$, $\gamma = 90.1(1)°$, $V = 1\,364.9$ Å^3, space group $P\bar{1}$, $Z = 4$, $D_x = 1.10$ g cm^{-3}, $F(000) = 496$, $\lambda = 1.5418$ Å, colourless square prisms, crystal dimensions 0.2 × 0.3 × 0.5 mm, μ(Cu-K_α) = 5.3 cm^{-1}.

Data Collection, Analysis, and Refinement.—CAD3 diffractometer, balanced filtered Cu-K_α radiation, $\theta/2\theta$ scan mode, scan width = (1.2 + 0.09 tan θ), 4 940 unique reflections measured ($2 \leqslant \theta \leqslant 67.5°$). Direct methods (MULTAN[11]). Least-squares refinement (SHELX[12]), non-hydrogen atoms anisotropic. All 42 methyl hydrogens located in difference Fourier, included with idealised geometries and common isotropic temperature factor which refined to $U = 0.12$ Å^2. Hydroxy hydrogens not located but included in final cycles along O(oxime) ··· O′(nitrone) lines with O–H distance fixed at 1.0 Å and $U_{iso} = 0.10$ Å^2 (fixed). For 2 925 reflections [$I > 6\sigma(I)$], final $R = 0.096$.

^{1}H and ^{13}C n.m.r. spectra were recorded using Bruker WH-90 and Bruker WM-250 instruments, respectively. Unless stated otherwise the chemical shifts were determined with $CDCl_3$ solvent using tetramethylsilane as reference. Mass spectra were recorded on an A.E.I. MS902 mass spectrometer (updated by V. G. Instruments Ltd.) using a heated inlet system and operating at 70 eV.

Kinetic studies of the thermal elimination of nitrones were carried out using a Unicam SP800 spectrophotometer. The disappearance of nitrone from a heated solution was monitored by the decrease in intensity of absorption at 275 nm in spectroscopic grade solvents. Experiments were carried out in a water-jacketted quartz cell over the temperature range 60—80 °C ± 0.1 °C.

Formation of Compounds (**2a**), (**3a**), *and* (**2b**).—The imino ketone (**2a**) and di-imines (**3a**) and (**3b**) were obtained by condensation of 2,2,4,4-tetramethylcyclobutane-1,3-dione with the appropriate amine in the presence titanium chloride catalyst as previously reported.[2]

Formation of Compounds (**5a**), (**5b**), *and* (**8a**).—The keto nitrone (**8a**) and dinitrones (**5a**) and (**5b**) were obtained by *m*-chloroperoxybenzoic acid oxidation of the corresponding imines in dichloromethane at *ca.* 5 °C over a period of 2 h. The nitrones were purified by column chromatography on silica gel using hexane–ether, methanol–ether mixtures as eluant. Yields were within the range 50—55%.

N-(2,2,4,4-*Tetramethyl*-3-*oxocyclobutylidene*)-*t-butylamine* N-*oxide* (**8a**). M.p. 71 °C (from pentane). (Found: C, 68.1; H, 10.2; N, 6.6. $C_{12}H_{22}NO_2$ requires C, 68.2; H, 10.0; N, 6.6%); δ_H (90 MHz; $CDCl_3$) 1.47 (6 H, s, Me), 1.52 (6 H, s, Me), and 1.56 (9 H, s, Bu^t).

N,N′-(2,2,4,4-*Tetramethylcyclobutanediylidene*)*bis-t-butylamine*- N,N′-*dioxide* (**5a**). M.p. 106 °C (from benzene–pentane) (Found: C, 69.7; H, 10.8; N, 9.75. $C_{16}H_{30}N_2O_2$ requires C, 68.0; H, 10.7; N, 9.2%); δ_H (90 MHz; $CDCl_3$) 1.56 (18 H, s, Bu^t) and 1.76 (12 H, s, Me); δ_C (62.9 MHz; $CDCl_3$) 20.5 (C-3), 28.8 (C-5), 55.9 (C-2), 70.7 (C-4), and 151.7 (C-1).

N,N′-(2,2,4,4-*Tetramethylcyclobutanediylidene*)*bisisopropylamine*-N,N′-*dioxide* (**5b**). M.p. 119—122 °C (from benzene–pentane) (Found: C, 66.4; H, 10.3, N, 10.85. $C_{14}H_{26}N_2O_2$ requires C, 66.1; H, 10.3; N, 11.0%); δ_H (250 MHz; $CDCl_3$) 1.43 [12 H, d, *J* 7 Hz, C(*Me*)$_2$H], 1.66 (12 H, s, Me), and 4.02 [2 H, sep *J* 7 Hz, C(Me)$_2$*H*]; δ_C (69.2 Hz; $CDCl_3$) 19.9 (C-3), 19.9 (C-5), 51.3 (C-2), 60.6 (C-4), and 149.9 (C-1).

Thermal Elimination Reactions of Nitrones (**5a**), (**6a**), *and* (**8a**).—Oxime products were obtained by heating the parent nitrone either in a sealed tube [(**2a**) and (**5a**)] or in toluene solution [(**5a**), (**6a**), and (**6b**)] at a specified temperature.

2,2,4,4-*Tetramethylcyclobutane*-1,3-*dione* 1-*oxime* (**9**). Heating the keto nitrone (**8a**) at 150 °C in a sealed tube for 1 h yielded the keto oxime (**9**) (96%), m.p. 137—139 °C (lit.,[13] m.p. 142—144 °C); δ_H (90 MHz; $CDCl_3$) 1.36 (6 H, s, Me), 1.48 (6 H, s, Me), and 8.24 (1 H, s, OH).

2,2,4,4-*Tetramethycyclobutane*-1,3-*dione* 1,3-*dioxime* (**7**). Heating the dinitrone (**5a**) under identical conditions to the keto nitrone (**8a**) gave the dioxime (**7**), in 99% yield, m.p. 280 °C (lit.,[14] m.p. 281 °C); δ_H (90 MHz; $CDCl_3$–$C_6D_6CD_3$) 2.10 (12 H, s, Me) and 5.15 (2 H, s, OH).

3-(*Hydroxyimino*)-N,N′-(2,2,4,4-*tetramethylcyclobutylidene*)-*t-butylamine* N-*oxide* (**6a**). Dinitrone (**5a**) was heated in toluene at 110 °C for 5 min to give compound (**6a**) as an insoluble crystalline product in 94% yield, m.p. 147—150 °C (decomp.) (Found: M^+, 226.168 34. $C_{12}H_{22}N_2O_2$ requires *M*, 226.168 11); δ_H (90 MHz; $CDCl_3$–C_6D_6) 1.36 (9 H, s, Bu^t), 1.57 (6 H, Me), 1.63 (6 H, s, Me), and 8.5 (1 H, s, OH); δ_C [62.81 MHz; $(CD_3)_2CO$] 21.2 (C-3/C-3′), 23.6 (C-3/C-3′), 28.7 (C-5), 52.1 (C-2/C-2′), 56.8 (C-2/C-2′), 70.2 (C-4), 153.1 (C-1), and 164.3 (C-1′). When the hydroxyimino nitrone (**6a**) was heated above the melting point, bubbles of 2-methylpropene were evolved and the dioxime (**7**) was formed.

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* *Supplementary data* (see Section 5.6.3 of Instructions for Authors in the January issue). Lists of fractional atomic co-ordinates, H-atom co-ordinates, thermal parameters, bond angles and lengths have been deposited at the Cambridge Crystallographic Data Centre.