# Rearrangement Reactions of Oxaziridines to Nitrones. X-Ray Crystal and Molecular Structure of *N*-t-Butyl-α(*o*-hydroxyphenyl)nitrone

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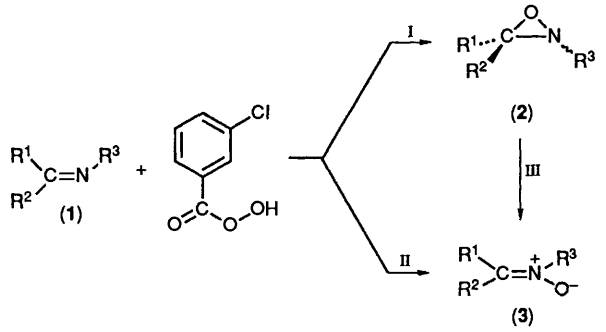
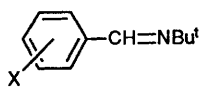
Substituted *N*-benzylidene-t-butylamines are oxidized with *m*-chloroperoxybenzoic acid to oxaziridines which can rearrange to the corresponding nitrones when electron-donating groups are present in the phenyl ring. The oxaziridine-to-nitrone rearrangement, which has been considered as a 'pseudo-abnormal' reaction, can also be catalysed by Lewis acids, It has been found that the rearrangement of 2-t-butyl-3-(*o*-hydroxyphenyl)oxaziridine to the corresponding nitrone is of first order. The rearrangement has been investigated for different substituents in the phenyl ring, and in the case of 2-t-butyl-3-phenyloxaziridine substituted in the *ortho* position with electron-donating groups it has been found that the presence of protons or a Lewis acid is necessary. An X-ray structure of α-(*o*-hydroxyphenyl)-*N*-t-butylnitrone shows strong hydrogen bonding between the nitrone oxygen and the hydrogen in the hydroxy group. The oxaziridine-to-nitrone rearrangement is also analysed from a theoretical point of view using *ab initio* calculations. A Mulliken-population analysis of the C–O and N–O bonds in the oxaziridine ring for *para*-substituted 2-t-butyl-3-phenyloxaziridines shows a reduction of the C–O bond population when an electron-donating group is present in the *para* position of the phenyl ring compared with an electron-withdrawing group; the N–O bond populations show the reverse picture. A state-correlation diagram for the oxaziridine-to-nitrone rearrangement is also presented and the experimental and theoretical results support each other.

The oxidation of imines (**1**) by peroxyacids normally affords the corresponding oxaziridines (**2**) (Route I, Scheme 1).[1]




**Scheme 1.**

As to the mechanism for the formation of oxaziridines (**2**) from imines (**1**) both experimental[2] and theoretical investigations[3] indicate that the reaction proceeds in a two-step fashion: nucleophilic attack of the peroxyacid at the imino carbon, followed by an intramolecular nucleophilic displacement. Nitrones (**3**) have also (in a few cases) been formed by the peroxyacid oxidation of imines (Route II, Scheme 1).[2a,4] The latter reaction has especially been observed in systems where electron-donating groups are attached to one of the substitutents on the imino carbon, or in systems where steric effects hinder the approach of the peroxyacid to the imino carbon in the plane perpendicular to the C=N bond.[4c] The rearrangement of oxaziridines (**2**) to nitrones (**3**) (Route III, Scheme 1) can be initiated photochemically,[5] but the thermal rearrangement has been observed in a few cases and is considered as a 'pseudo-abnormal' reaction.[4c] A kinetic study of the thermal rearrangement of oxaziridine to nitrone showed that the reaction was first order, and that the rearrangement was facilitated by electron-donating substituents on the phenyl ring.[6] During the refereeing process of this paper Boyd *et al.* published a study of the synthesis of nitrones by imine oxidation using either a peroxy acid or dimethyldioxirane.[7] It was, for example, found that both *C*-aryl substituents and electron-donating groups in the *para* position of the *C*-aryl substituent facilitated the formation of nitrones.[7]




(**1a–g**)

In this paper we want to show that the rearrangement of oxaziridines (**2**) to nitrones (**3**) (Route III, Scheme 1) is a common reaction observed in the oxidation of phenyl-substituted *N*-benzylidene-t-butyl amines (**1a–g**). Electron-donating substituents in the phenyl ring favour this rearrangement. Furthermore, it will be shown that the oxaziridine-to-nitrone rearrangement can be catalysed by Lewis acids. In an attempt to throw some light on the mechanism for the rearrangement (**2**) ⟶ (**3**) a crystal structure of one of the nitrones has been obtained and we have performed a series of *ab initio* calculations.

## Results and Discussion

*Experimental Results.*—A series of different imines (**1a–h**) has been treated with *m*-chloroperoxybenzoic acid (MCPBA) in methylene dichloride at 20 °C (for further experimental details see Experimental section). The results are given in Table 1.

It appears from the experimental results in Table 1 that the oxaziridine (**2**) is the major product after 2.5 h, except for the case of (**1e**) where 57% of the nitrone (**3e**) is formed after 2.5 h.

**Table 1.** Oxidation of imines (**1a–h**) with MCPBA in methylene dichloride at 20 °C.[a]

| Imine (**1**) | Reaction time (h) | Oxaziridine (**2**) (yield/%) | Nitrone (**3**) (yield/%) | Other products (% yield) |
|---|---|---|---|---|
| (**1a**) PhCH=NBu$^t$ | 2.5 | 97 | | PhCHO (3) |
| | 72 | 85 | | PhCHO (12), PhC(O)NHBu$^t$ (3) |
| (**1b**) *p*-$O_2NC_6H_4CH$=NBu$^t$ | 2.5 | 100 | | |
| | 72 | 100 | | |
| (**1c**) *p*-$MeOC_6H_4CH$=NBu$^t$ | 2.5 | 92 | 4 | *p*-$MeOC_6H_4CHO$ (4) |
| | 72 | 46 | 44 | *p*-$MeOC_6H_4CHO$ (10) |
| (**1d**) *o*-$MeOC_6H_4CH$=NBu$^t$ | 2.5 | 93 | 2 | *o*-$MeOC_6H_4CHO$ (5) |
| | 72 | 93 | 2 | *o*-$MeOC_6H_4CHO$ (5) |
| (**1e**) *p*-$HOC_6H_4CH$=NBu$^t$ | 2.5 | 4 | 57 | *p*-$HOC_6H_4CHO$ (5) |
| | | | | *p*-$HOC_6H_4C(O)NHBu^t$ (16) |
| | 72 | | 22 | *p*-$HOC_6H_4CHO$ (6) |
| | | | | *p*-$HOC_6H_4C(O)NHBu^t$ (21) |
| (**1f**) *o*-$HOC_6H_4CH$=NBu$^t$ | 2.5 | 31 | 6 | *o*-$HOC_6H_4CHO$ (2) |
| | | | | *o*-$HOC_6H_4C(O)NHBu^t$ (9) |
| | 72 | | 40 | *o*-$HOC_6H_4CHO$ (5) |
| | | | | *o*-$HOC_6H_4C(O)NHBu^t$ (8) |
| (**1g**) *m*-$HOC_6H_4CH$=NBu$^t$ | 2.5 | 100 | | |
| | 72 | 99 | trace | |
| (**1h**) Ph(Et)C=NPh | 2.5 | | | Ph(Et)C=O (68) |
| | | | | $EtC(O)NPh_2$ (22) |
| | | | | (**4h**) |
| | | | | PhC(O)NPh(Et) (10) |
| | | | | (**4h′**) |

[a] See Experimental section for details.

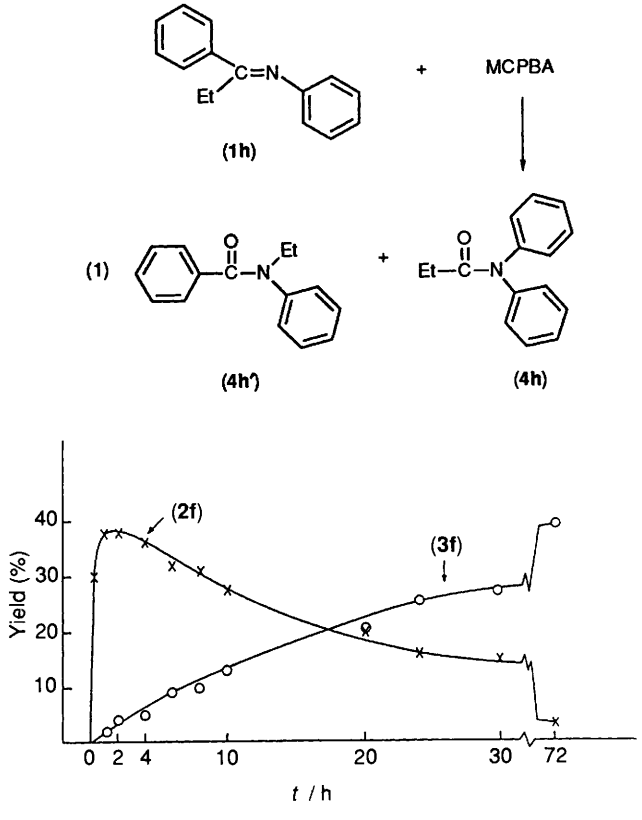



**Figure 1.** The change in product distribution of the oxaziridine (**2f**) and the nitrone (**3f**) in the reaction of the imine (**1f**) with MCPBA.

However, in the case of substrates (**1c**) and (**1f**) a significant amount of the corresponding nitrone is formed after 72 h. The ketimine (**1h**) gives, beside the ketone cleavage product, two rearranged amide products (**4h**) and (**4h′**) [equation (1)], which could indicate a Baeyer–Villiger-type of rearrangement under these reaction conditions.

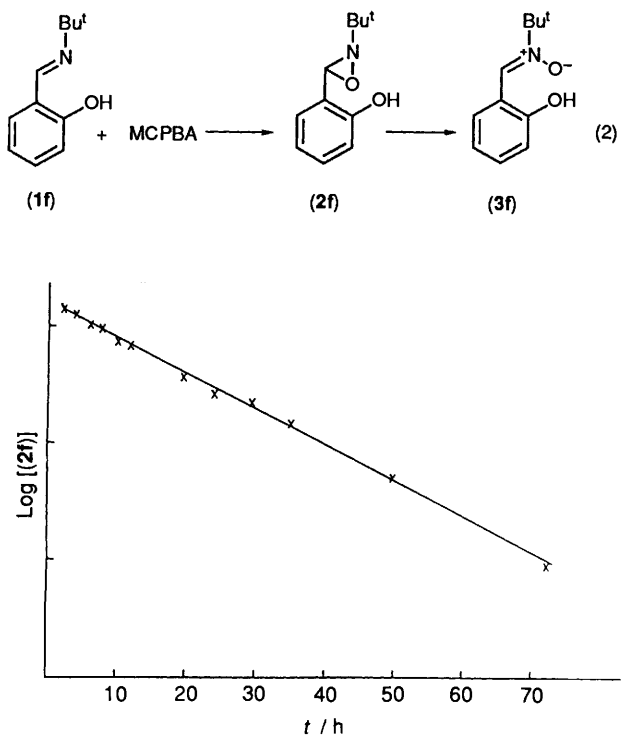



**Figure 2.** log[(**2f**)] as a function of time.

The reaction of imine (**1f**) with MCPBA at 20 °C has been studied as a function of time and the yield of the oxaziridine (**2f**), and the nitrone (**3f**) is shown in Figure 1. It appears from Figure 1 that the oxaziridine (**2f**) is formed in nearly 40% yield after 0.5 h, after which it disappears due to the formation of the nitrone (**3f**). The curves in Figure 1 show thus that the oxaziridine (**2f**) is formed first, and then rearranges to the nitrone (**3f**) [equation (2)].

Figure 2 shows log[**2f**] as a function of time. The straight line indicates that the rearrangement is first order. The reaction rate

**Table 2.** Rearrangement of oxaziridines (**2a–d** and **f**) to nitrones (**3a–d** and **f**) catalysed by Lewis acids.[a]

| Oxaziridine (2) | Lewis acid[b] | Reaction time (h) | Nitrone (3) (yield/%) | Other products (yield/%) |
|---|---|---|---|---|
| (**2a**) PhCH-NBu$^t$ | DCl | 20 | | |
| | $AlCl_3$ | 24 | 74 | PhCHO (26) |
| (**2b**) *p*-$O_2NC_6H_4$CH-NBu$^t$ | DCl | 22 | | |
| | $AlCl_3$ | 22 | 11 | *p*-$O_2NC_6H_4CHO$ (22) |
| (**2c**) *p*-$MeOC_6H_4$CH-NBu$^t$ | DCl | 1 | 12 | *p*-$MeOC_6H_4CHO$ (17) |
| | | 24 | 31 | *p*-$MeOC_6H_4CHO$ (33) |
| | $AlCl_3$ | 1 | 78 | *p*-$MeOC_6H_4CHO$ (22) |
| (**2d**) *o*-$MeOC_6H_4$CH-NNBu$^t$ | DCl | 24 | 12 | *o*-$MeOC_6H_4CHO$ (2) |
| | $AlCl_3$ | 24 | 89 | *o*-$MeOC_6H_4CHO$ (11) |
| (**2f**) *o*-$HOC_6H_4$CH-NBu$^t$ | DCl | 2 | 6 | *o*-$OHC_6H_4CHO$ (8) |
| | $AlCl_3$ | 24 | 83 | *o*-$OHC_6H_4CHO$ (17) |

[a] See Experimental section for details. [b] (**2**): Lewis acid 1:1.

constant is calculated to be $2.5 \times 10^{-5}$ $s^{-1}$, which is in good agreement with the results obtained by others.[6] Thus, the rearrangement (**2f**) ⟶ (**3f**) is independent of the *m*-chlorobenzoic acid and MCPBA.

Imines with a hydrogen (**1a**) or a nitro group (**1b**) attached to the *para*-position in the phenyl ring are oxidized to the oxaziridines, which do not rearrange to the nitrones. However, imines with an electron-donating group attached to either the *ortho*- or *para*-position in the phenyl ring, (**1c**) and (**1f**), are first oxidized to the oxaziridines by reaction with MCPBA, followed by a rearrangement of the oxaziridines to the nitrones. The oxaziridine-to-nitrone rearrangement is, in the case of electron-donating groups present in the *ortho*-position of the phenyl ring, dependent on the accessibility of a proton. The *ortho*-hydroxy derivative (**2f**) rearranges to the nitrone (**3f**) whereas the *ortho*-methoxy derivative (**2d**) forms only the nitrone (**3d**) in small amounts under similar reaction conditions. The results in Table 1 show that two factors seem to be of importance for the oxaziridine-to-nitrone rearrangement: an electronic factor and an acidic one.

We have thus studied the rearrangement of oxaziridines (**2a–d** and **f**) to nitrones (**3a–d** and **f**) in the presence of protons or a Lewis acid (aluminium trichloride.)* The results are given in Table 2.

The results in Table 2 show that it is possible to achieve the oxaziridine (**2a–d** and **f**)-to-nitrone (**3a–d** and **f**) rearrangement by the addition of protons or a Lewis acid. The major by-product in these rearrangement reactions is the aldehyde formed by cleavage of the oxaziridine function. Aluminium trichloride is found to be a better catalyst for the rearrangement compared with deuterium chloride. The former is able to achieve the rearrangement of (**2b**) ⟶ (**3b**), where an electron-withdrawing group is attached to the *para*-position in the phenyl group. It should also be noted that the rearrangement of (**2f**) ⟶ (**3f**) is not catalysed further by the addition of one mol equivalent of DCl. These results indicate that the proton in the hydroxy group of compound (**2f**) is located in an optimal position for catalysing the rearrangement. It appears also that the *ortho*-methoxy derivative (**2d**) is, in the presence of a Lewis acid, able to rearrange to the nitrone (**3d**) in high yield compared with the uncatalysed reaction. These results show that in the case of oxaziridines substituted with electron-donating groups in the *ortho*-position of the phenyl ring, (**2d** and **f**), a Lewis acid is necessary for the rearrangement to take place, whereas this is not the case for oxaziridines substituted with electron-donating groups in the *para*-position of the phenyl ring, (**2c** and **e**),

In an attempt to obtain further insight in the oxaziridine-to-nitrone rearrangement we have obtained an X-ray structure of the nitrone (**3f**) as shown in Figure 3.

Three points of interest arise from the structure of compound (**3f**): (i) the hydrogen in the hydroxy group points towards the oxygen in the nitrone, (ii) the short $O^2 \cdots H^1$ distance[9] ($O^1 \cdots O^2$ 2.47 Å) of 1.53 Å, showing strong hydrogen bonding of the hydrogen in the hydroxy group to the oxygen in the nitrone function, (iii) the nitrone oxygen ($O^2$) is tilted 27° out of the $O^1$–phenyl–$C^1$ plane (for further data see Table 5). The two first points show that the hydrogen in the hydroxy group might be involved in the rearrangement at some stage of the reaction path. The out-of-plane $O^2$ maximizes the interaction of the lone-pair electrons on $O^2$ with $H^1$ (see *Theoretical Results*).

*Theoretical Results.*—The oxaziridine-to-nitrone rearrangement can be initiated photochemically and several papers have dealt with the photochemical as well as acid-catalysed ring opening of oxaziridines[10,11] The theoretical work concerning the acid-catalysed ring opening of oxaziridines focuses mainly on the protonation sites of the oxaziridine.[11] The transformation of the unsubstituted oxaziridine into the nitrone can proceed by one of two typical reaction paths.[10a] The first one consists in a direct transformation with simultaneous C–O bond breaking–ring opening and methylene-group rotation. The second one is a two-step process [equation (3)]. First, the ring is opened through C–O bond breaking to give a CNO angle close to 110°. Then the methylene group rotates from a perpendicular to a CNO-in-plane position. Theoretical calculations have shown that the direct transformation requires much more energy than the two-step process.[10a]

The *thermal* rearrangement [equation (3)] requires an

* Nitrones have been observed in a few cases when oxaziridines have been in contact with a Lewis acid (silica gel).[8]

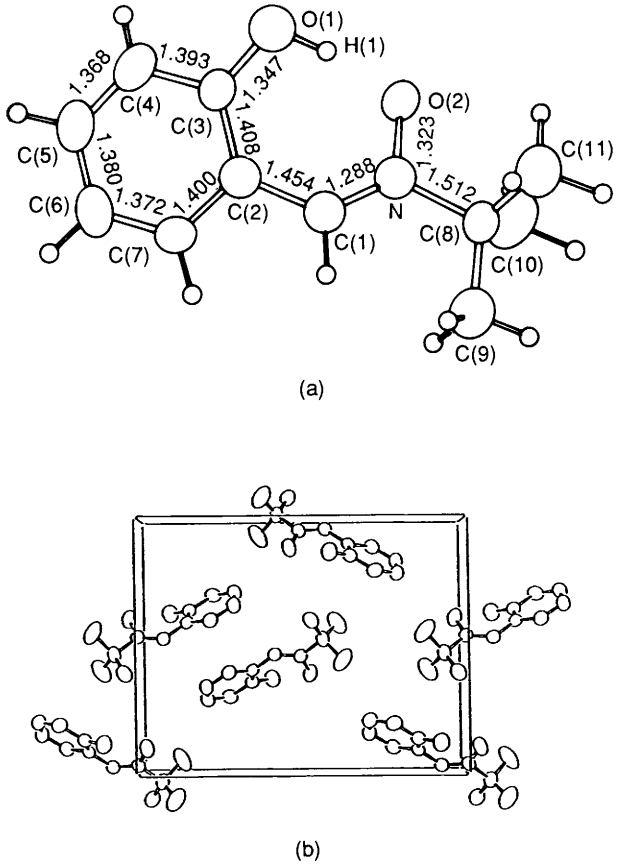



**Figure 3.** (a) The X-ray molecular structure of the nitrone (**3f**). (b) The unit cell.

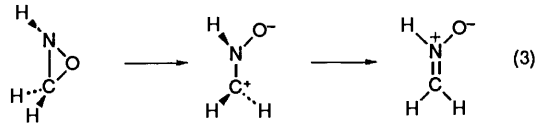



**Table 3.** Some electronic properties of compounds (**2a, b,** and **e**) (only for the oxaziridine ring).

| | (2a) | (2b) | (2e) |
|---|---|---|---|
| Atomic charge | | | |
| O | −0.161 | −0.154 | −0.163 |
| N | −0.180 | −0.176 | −0.183 |
| Mulliken-population analysis | | | |
| C–O | 0.1826 | 0.1831 | 0.1820 |
| N–O | 0.1314 | 0.1260 | 0.1334 |
| HOMO energy (eV) | −8.00 | −8.38 | −6.69 |

activation barrier of 58 kcal mol$^{-1}$ * at the STO-3G level of calcuations.[10a] The *photochemical* rearrangement is described as taking place *via* either an $S_0$ or a $T_1$ excited state.[10a] Our intention with the theoretical calculation here is two-fold. First we want to show why the oxaziridines with an electron-donating group attached to the *para* position in the phenyl group, *e.g.* (**2e**), rearranges more readily than the system with an electron-withdrawing group, (**2b**). Second, we want to show why Lewis acids catalyse the oxaziridine-to-nitrone rearrangement (**2d** and **f**) ⟶ (**3d** and **f**). For these purposes we have used *ab initio* calculations.[12]

The structures of the ground state of isomers (**2a**) and (**3a**) have been optimized at the STO-3G* level of calculations (it should be noted that we have used a methyl group instead of the t-butyl group in our calculations). The optimized structures of compounds (**2a**) and (**3a**) are in good agreement with standard bond lengths and angles for these types of compounds.† The optimized structures for compounds (**2a**) and (**3a**) were then used for the calculation of the electronic properties of their analogous (**2b** and **e**) and (**3b** and **e**) where the hydrogen in the *para* position in the phenyl ring was replaced with a nitro [(**2b**), (**3b**)] or a hydroxy [(**2e**), (**3e**)] group. Table 3 shows the atomic net charges on the oxygen and the nitrogen, Mulliken-population analysis for the C–O and N–O bonds in the oxaziridine ring, and the energy of the highest occupied molecular orbital (HOMO) located on the oxaziridine ring in compounds (**2a, b,** and **e**).

Inspection of the results in Table 3 shows that the charges on the oxygen and the nitrogen in the oxaziridine ring in compounds (**2a, b,** and **e**) are not affected very much by changing of the substituent in the *para* position in the phenyl ring from electron-withdrawing (**2b**) to electron-donating (**2e**) compared with hydrogen. The Mulliken-population analysis shows that the C–O bond is strongest in (**2b**) and weakest in (**2e**), whereas the reverse picture is observed for the N–O bond; these results indicate that the easiest C–O bond to break is in compound (**2e**). The HOMO results show that compound (**2e**) has the highest energy (−6.69 eV) and (**2b**) has the lowest (−8.38 eV). Assuming that the interaction between the Lewis acid and the oxaziridine leading to the rearrangement is initiated by an interaction of the HOMO of the oxaziridine and the LUMO of the proton/Lewis acid, it appears from the results in Table 3 that the oxaziridine with an electron-donating group present in the *para*-position in the phenyl ring is able to interact in a much more favourable way with an electrophile compared with oxaziridines with a *para* electron-withdrawing group. These results might to a certain extent account for the observed rearrangement of oxaziridines to nitrones. However, let us also here try to investigate the rearrangement in terms of a correlation diagram where the notation from Bigot *et al.* has been applied.[10a]

The total energy of the ground state of compounds (**2a, b,** and **e**) is −431.976, −632.665, and −505.817 au‡, respectively as shown in Figure 4 [the total energy of the oxaziridines (**2a, b,** and **e**) is chosen as the zero point]. The total energy of the ground state of the nitrones (**3a, b,** and **e**) is shown relative to the total energy of the oxaziridines as the three lowest energy levels to the right in Figure 4. The total energy of the electronic states of the nitrones correlating with the ground state of the oxaziridines (**2a, b,** and **e**) is shown as the three highest energy levels to the right in Figure 4 (**3a′, b′,** and **e′**). The total energy of the states of the oxaziridines which correlate with (**3a, b,** and **e**) is shown as (**2a′, b′,** and **e′**), the three highest energy levels to the left in Figure 4, a simplified state-correlation diagram for the rearrangement of oxaziridines (**2a, b,** and **e**) to nitrones (**3a, b,** and **e**).

The state-correlation diagram for the isomerisation (**2a, b,** and **e**) ⟶ (**3a, b,** and **e**) shown in Figure 4 offers an explanation as to why, *e.g.* (**2e**) rearranges much more readily to (**3e**) than does (**2b**) to (**3b**). The activation barrier for the rearrangement of (**2e**) ⟶ (**3e**) can be estimated to be 15–20 kcal mol$^{-1}$, whereas the activation barrier for (**2b**) ⟶ (**3b**) is 45–50 kcal mol$^{-1}$ at the STO-3G* level of calculations. The activation energies for the rearrangements (**2a**) ⟶ (**3a**) and

* 1 cal = 4.184 J.

† The structure of the oxaziridine and nitrone moiety in the optimized systems compares well with the X-ray structural data.[13]

‡ 1 a.u. = 27.21 eV.

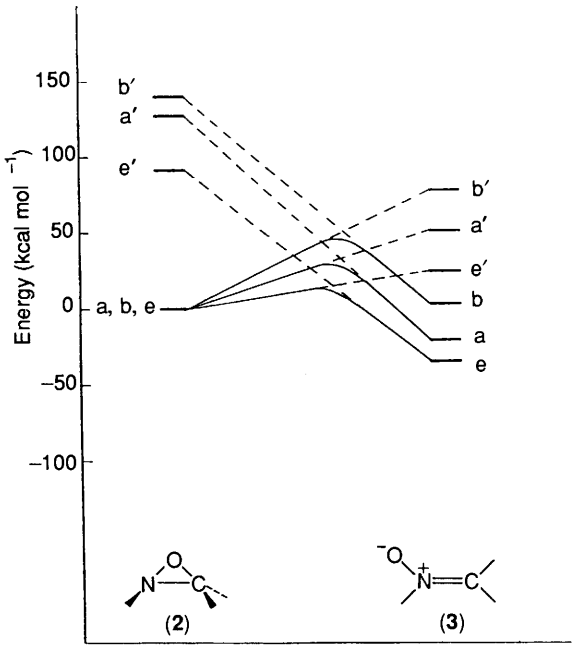
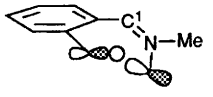



**Figure 4.** A simplified state-correlation diagram for the rearrangement of (**2a**, **b**, and **e**) to (**3a**, **b**, and **e**).

(**2e**) ⟶ (**3e**) are in good agreement with the results obtained by Boyd *et al.*,[6] whereas the activation energy for (**2b**) ⟶ (**3b**) is ~15 kcal mol$^{-1}$ higher. The rearrangement (**2a** and **e**) ⟶ (**3a** and **e**) is exothermic by ~20 and 32 kcal mol$^{-1}$, respectively, whereas that for (**2b**) ⟶ (**3b**) is endothermic by ~4 kcal mol$^{-1}$.

From the X-ray structure of the nitrone (**3f**) (Figure 3) it appears that the nitrone oxygen is tilted 27° out of the O$^1$–phenyl–C$^1$ plane and that it points towards the hydrogen in the hydroxy group. The total energy of compound (**3f**) (−505.865 au) is 19 kcal mol$^{-1}$ lower than in the corresponding planar system. One of the lone pairs on the nitrone oxygen is located in such a way that it maximizes overlap with the $\sigma^*_{O-H}$ when the oxygen is titled out of the O$^2$–phenyl–C$^1$ plane as shown in structure (**5**).




(**5**)

The results for the rearrangement of compounds (**2d**) and (**3f**) show that the accessibility of a Lewis acid to the reagent plays an important role in the rearrangement. The oxaziridine oxygen in compound (**2f**) is located perpendicular to the phenyl–carbon–nitrogen plane (STO-3G* optimized structure). The total energy of compound (**2f**) is −505.832 au, showing that the nitrone (**3f**) is 21 kcal mol$^{-1}$ more stable than the oxaziridine. The hydroxy hydrogen–oxaziridine oxygen distance in compound (**2f**) is 2.35 Å, indicating that the overlap is negligible. A rotation of 45° of the oxaziridine group towards the hydroxy group to favour H–O interaction leads to a decrease in C–O population by 0.047. By the same rotation angle the N–O population shows an increase of 0.032. The decrease in C–O population is mainly caused by donation of electron density from a C–O bonding orbital into an unoccupied H–O orbital in the hydroxy group. This H–O interaction is the one which at a later stage in the reaction is responsible for the strong hydrogen bond in the nitrone (**3f**).

*Conclusion.*—The present results indicate that the oxaziridine-to-nitrone rearrangement (Route III, Scheme 1) can, for some systems, be considered as a common rather than a 'pseudo-abnormal' reaction. The arrangement proceeds rather well in the MCBPA oxidation of phenyl-substituted *N*-benzylidene-t-butylamines (**1**) substituted with electron-donating groups in the phenyl ring. The oxaziridine-to-nitrone rearrangement often proves a high activation barrier. The systems with an electron-donating group attached to the phenyl ring studied here undergo a rearrangement, probably because the electron-donating group lowers the activation barrier compared with the electron-withdrawing group and because the reaction in the former case is slightly exothermic. However, the oxaziridine with an electron-withdrawing group needs a catalyst to overcome the activation barrier for the rearrangement to the nitrone. The oxaziridine-to-nitrone rearrangement is a general reaction for the systems studied here when protons or Lewis acids are present. The oxidation of *N*-(*o*-hydroxybenzylidene)-t-butylamine (**1f**) with MCPBA affords rapid formation of the corresponding oxaziridine (**2f**), followed by a slow intramolecular rearrangement to the nitrone (**3f**). The driving force in the (**2f**) ⟶ (**3f**) rearrangement is probably the hydrogen (proton) in the hydroxy group which interacts with the oxaziridine oxygen. This interaction causes a weakening of the carbon–oxygen bond. The hydrogen (proton) in the hydroxy group catalyses the rearrangement to the nitrone, leading to a strong hydrogen bond between the oxygen in the nitrone function and the hydrogen in the hydroxy group.

## Experimental

$^1$H NMR spectra were recorded on a Varian Gemini 200 spectrometer. $SiMe_4$ was used as internal standard. Mass spectra were recorded on a MicroMass 7070F or Trio-2 spectrometer operating at 70 eV with a direct inlet.

*Materials.*—All the imines and oxaziridines were synthesized according to the literature.[1a,b,14] Solvents and other materials were used as received from the company.

*General Procedure for the Oxidation of Imines by MCPBA.*—The imine (2.5 mmol) was dissolved in $CH_2Cl_2$ (2 ml). A solution of MCPBA (2.5 mmol) in $CH_2Cl_2$ (8 ml) was added and the reaction mixture was stirred for 2.5 h or 72 h at room temperature. The thus formed *m*-chlorobenzoic acid was removed by filtration. The filtrate was washed first with aq. sodium sulphite and then with aq. sodium carbonate. The organic phase was dried over sodium carbonate and the solvent was evaporated off. The products formed were determined by $^1$H NMR spectroscopy. The $^1$H NMR data, all in $CDCl_3$, are given below:

(**1a**) δ 1.30 (s, 9 H, Bu$^t$), 8.27 (s, 1 H, CH=N), and 7.37–7.40 and 7.72–7.77 (m, 5 H, Ph).

(**2a**) δ 1.18 (s, 9 H, Bu$^t$), 4.68 (s, 1 H, CHN), and 7.35–7.48 (m, 5 H, Ph).

(**3a**) δ 1.62 (s, 9 H, Bu$^t$), 7.55 (s, 1 H, CH=N), and 7.40–7.43 and 8.27–8.32 (m, 5 H, Ph).

(**1b**) δ 1.32 (s, 9 H, Bu$^t$), 8.34 (s, 1 H, CH=N), 7.92 (d, 2 H, ArH), and 8.27 (d, 2 H, ArH).

(**2b**) δ 1.20 (s, 9 H, Bu$^t$), 4.78 (s, 1 H, CHN), 7.63 (d, 2 H, ArH), and 8.23 (d, 2 H, ArH).

(**3b**) δ 1.61 (s, 9 H, Bu$^t$), 8.10 (s, 1 H, CH=N), 8.12 (d, 2 H, ArH), and 8.19 (d, 2 H, ArH).

(**1c**) δ 1.28 (s, 9 H, Bu$^t$), 3.83 (s, 3 H, MeO), 8.22 (s, 1 H, CH=N), 6.92 (d, 2 H, ArH), and 7.69 (d, 2 H, ArH).

(**2c**) δ 1.17 (s, 9 H, Bu$^t$), 3.80 (s, 3 H, MeO), 4.64 (s, 1 H, CHN), 6.89 (d, 2 H, ArH), and 7.37 (d, 2 H, ArH).

(**3c**) δ 1.60 (s, 9 H, Bu$^t$), 3.82 (s, 3 H, MeO), 7.48 (s, 1 H, CH=N), 6.92 (d, 2 H, ArH), and 8.30 (d, 2 H, ArH).

**Table 4.** Experimental parameters for the X-ray diffraction study of compound (**3f**).

| | |
|---|---|
| Colour and form | Pale yellow needles |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| $a$ (Å) | 15.478(5) |
| $b$ (Å) | 12.054(3) |
| $c$ (Å) | 5.849(1) |
| $V$ (Å$^3$) | 1 091.2 |
| Crystal size (mm) | 0.15 × 0.1 × 0.05 |
| Radiation | Mo-$K_\alpha$ |
| Reflections collected | 1 161 |
| Reflections with $I > 3\,\sigma(I)$[a] | 729 |
| $R$-factor | 0.037 |
| $R_w$ | 0.042 |
| GOF[b] | 1.48 |
| Structure solution | MULTAN |

[a] Corrections: Lorentz and polarization. [b] Goodness-of-fit.

**Table 5.** Bond lengths (Å) and angles (°) for compound (**3f**).

| | | | |
|---|---|---|---|
| N–C(1) | 1.288(5) | C(1)–N–O(2) | 122.6(4) |
| N–O(2) | 1.323(4) | N–C(1)–C(2) | 128.1(4) |
| C(1)–C(2) | 1.454(6) | C(1)–C(2)–C(7) | 115.5(4) |
| C(2)–C(3) | 1.408(6) | C(1)–C(2)–C(3) | 126.9(4) |
| C(3)–C(4) | 1.393(6) | C(3)–C(2)–C(7) | 117.6(4) |
| C(4)–C(5) | 1.368(7) | C(2)–C(3)–C(4) | 119.5(4) |
| C(5)–C(6) | 1.380(7) | C(3)–C(4)–C(5) | 120.8(5) |
| C(6)–C(7) | 1.372(6) | C(4)–C(5)–C(6) | 120.7(5) |
| C(2)–C(7) | 1.400(6) | C(5)–C(6)–C(7) | 118.9(5) |
| C(3)–O(1) | 1.348(5) | C(6)–C(7)–C(2) | 122.3(5) |
| C(8)–N | 1.512(6) | O(1)–C(3)–C(2) | 122.5(4) |
| C(8)–C(9) | 1.500(6) | O(1)–C(3)–C(4) | 118.0(4) |
| C(8)–C(10) | 1.536(9) | N–C(8)–C(9) | 111.9(4) |
| C(8)–C(11) | 1.513(8) | N–C(8)–C(10) | 106.5(5) |
| O(1)···O(2) | 2.473(4) | N–C(8)–C(11) | 106.7(4) |
| HO(1)–O(1) | 0.956(47) | C(9)–C(8)–C(10) | 107.6(5) |
| HO(1)–O(2) | 1.525(49) | C(9)–C(8)–C(11) | 111.7(5) |
| | | C(10)–C(8)–C(11) | 112.3(6) |
| | | C(3)–O(1)–HO(1) | 104.1(26) |
| | | C(3)–O(1)···O(2) | 98.3(3) |
| | | N–O(2)–HO(1) | 105.9(16) |
| | | O(2)–HO(1)–O(1) | 170.6(40) |

**Table 6.** Final fractional atomic co-ordinates ( × 10$^4$) for compound (**3f**) (non-hydrogen atoms only).

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| O(1) | 9 083(2) | 1 322(3) | 12 061(6) |
| O(2) | 10 307(2) | 1 100(3) | 9 381(6) |
| N | 10 003(2) | 393(3) | 7 850(7) |
| C(1) | 9 193(3) | 322(4) | 7 363(8) |
| C(2) | 8 480(3) | 954(3) | 8 328(8) |
| C(3) | 8 448(3) | 1 448(4) | 10 508(8) |
| C(4) | 7 718(4) | 2 047(5) | 11 149(10) |
| C(5) | 7 026(3) | 2 142(4) | 9 706(11) |
| C(6) | 7 025(3) | 1 617(4) | 7 608(10) |
| C(7) | 7 744(3) | 1 035(4) | 6 948(9) |
| C(8) | 10 697(3) | −280(4) | 6 674(9) |
| C(9) | 10 330(4) | −1 024(6) | 4 862(12) |
| C(10) | 11 297(5) | 556(9) | 5 489(18) |
| C(11) | 11 154(6) | −934(9) | 8 521(14) |

(**1d**) δ 1.29 (s, 9 H, Bu$^t$), 3.85 (s, 3 H, MeO), 8.71 (s, 1 H, CH=N), and 6.87–7.01, 7.30–7.38, and 7.94–7.99 (m, 4 H, ArH).

(**2d**) δ 1.19 (s, 9 H, Bu$^t$), 3.88 (s, 3 H, MeO), 5.14 (s, 1 H, CHN), and 6.87–7.00 and 7.28–7.36 (m, 4 H, ArH).

(**3d**) δ 1.61 (s, 9 H, Bu$^t$), 3.85 (s, 3 H, MeO), 8.06 (s, 1 H, CH=N), and 6.85–6.92, 7.28–7.42, and 9.32–9.43 (m, 4 H, ArH).

(**1e**) δ 1.34 (s, 9 H, Bu$^t$), 6.21 (s, 1 H, OH), 8.15 (s, 1 H, CH=N), 6.62 (d, 2 H, ArH), and 7.52 (d, 2 H, ArH).

(**3e**) δ 1.61 (s, 9 H, Bu$^t$), 6.3 (s, 1 H, OH), 7.55 (s, 1 H, CH=N), 6.86 (d, 2 H, ArH), and 8.17 (d, 2 H, ArH).

(**1f**) δ 1.29 (s, 9 H, Bu$^t$), 14.34 (s, 1 H, OH), 8.29 (s, 1 H, CH=N), and 6.76–6.92 and 7.20–7.29 (m, 4 H, ArH).

(**2f**) δ 1.21 (s, 9 H, Bu$^t$), 11 (br, 1 H, OH), 4.80 (s, 1 H, CHN), and 6.73–7.43 (m, 4 H, ArH).

(**3f**) δ 1.63 (s, 9 H, Bu$^t$), 12.37 (s, 1 H, OH), 7.72 (s, 1 H, CH=N), and 6.81–6.89, 6.95–7.00, 7.08–7.12, and 7.34–7.43 (m, 4 H, ArH).

(**1g**) δ 1.28 (s, 9 H, Bu$^t$), 7.65 (s, 1 H, OH), 8.19 (s, 1 H, CH=N), and 6.80–6.86 and 7.12–7.26 (m, 4 H, ArH).

(**2g**) δ 1.18 (s, 9 H, Bu$^t$), 6.1 (s, 1 H, OH), 4.70 (s, 1 H, CHN), and 6.77–7.00 and 7.15–7.26 (m, 4 H, ArH).

(**3g**) δ 1.63 (s, 9 H, Bu$^t$), 9.70 (s, 1 H, OH), 7.57 (s, 1 H, CH=N), and 6.86–6.97, 7.20–7.28, and 9.09–9.09 (m, 4 H, ArH).

(**4h**) δ 1.13 (t, 3 H, Me), 2.27 (q, 2 H, $CH_2$), and 7.23–7.41 (m, 10 H, 2 Ph).

(**4h′**) δ 1.22 (t, 3 H, Me), 3.92 (q, 2 H, $CH_2$), and 7.00–7.05 and 7.09–7.32 (m, 10 H, 2 Ph).

*Kinetic Study of Reaction of Compound* (**1f**) *with MCPBA.*—Compound (**1f**) (0.05 mmol) and MCPBA (0.05 mmol) were dissolved in $CDCl_3$ (1 ml) and the product distribution was followed by $^1$H NMR spectroscopy at 20 °C.

*Lewis Acid-catalysed Rearrangement of Oxaziridines to Nitrones.*—The oxaziridine (0.058 mmol) and DCl or $AlCl_3$ (0.058 mmol) were dissolved in $CDCl_3$ (1 ml) and the product distribution was analysed by $^1$H NMR spectroscopy.

*X-Ray Structure Analysis.*—The X-ray data for compound (**3b**) were collected at room temperature on a HUBER diffractometer with Nb-filtered Mo-$K_\alpha$ radiation; $2\theta < 50°$, $k > 0$, Cell dimensions determined from 31 reflections with $20 \leq 2\theta \leq 30°$, centred at $\pm 2\theta$ and at high and low $\chi$. Integration according to the method of Nelmes;[15] a 20% drop in intensity of two standard reflections was corrected for. Other experimental parameters are given in in Table 4. Refinement was by full-matrix least squares; non-hydrogen atoms were refined anisotropically, hydrogen atoms isotropically, giving 188 parameters. The weighting scheme used was $w = \{[\sigma(F^2) + 1.03F^2]^{\frac{1}{2}} - |F|\}^{-2}$.

Table 5 gives bond lengths and angles, and Table 6 gives final atomic co-ordinates.*

* *Supplementary data* (see section 5.6.3 of Instructions for Authors, in the January issue). Thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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