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Intramolecular Hydrogen Migration of Geometrically Constrained 3,3-Diphenyl-2-t-butyloxaziridine

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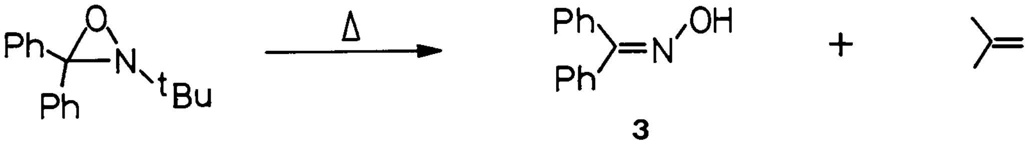
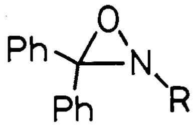
Thermolysis of 3,3-diphenyl-2-t-butyloxaziridine gave benzophenone oxime and isobutylene via the C-O bond fission followed by the intramolecular synchronous hydrogen migration from the t-butyl group without the intervention of the corresponding nitrone.

Although the Cope elimination reaction of tetrahedral N-oxides has been studied extensively,[1] the reaction of trigonal N-oxides (nitrones) is scarce. In those, Emmons et al.[2] reported on the vapor phase pyrolysis of 2-t-butyl-3-phenyloxaziridine, which gave the mixture of N-t-butyl-α-phenylnitrone, benzaldoxime, and isobutene with other small components. Recently, Boyd et al.[3] have shown that 3,3-diaryl-2-t-butyloxaziridines gave the corresponding substituted benzophenone oxime and isobutene upon thermolysis at 95 °C. A Cope-type elimination reaction in the nitrone formed initially was proposed for the formation of the oxime and olefin, however, no evidence for the intervention of the nitrone intermediate was presented.



1a **3**

Molecular model consideration of these oxaziridines made us to be aware that the direct hydrogen migration from the substituent at the 2-position is capable especially in a t-butyl group. Herein, we wish to report our studies on the thermal reaction of 3,3-diphenyl-2-alkyloxaziridines **1** and the corresponding nitrones **2**.



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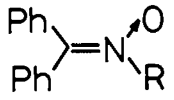


2

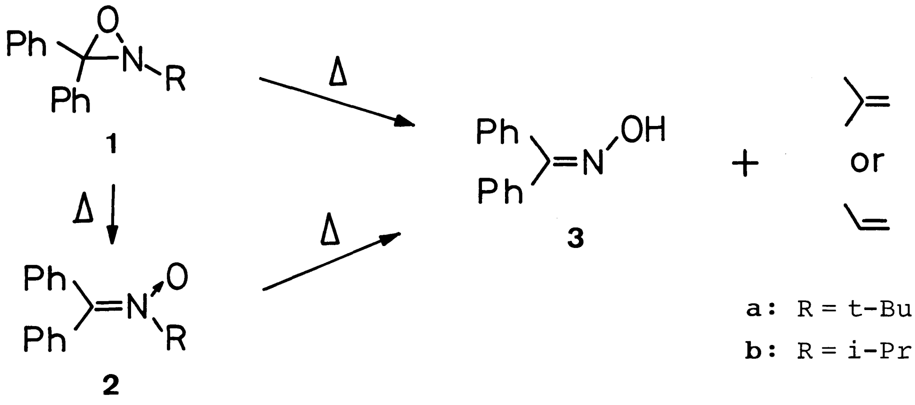
a: R = t-Bu
b: R = i-Pr
c: R = Et

Objectives **1** and **2** were prepared by the known procedures.4) A thermal reaction of **1** was remarkably dependent on the nature of the substituent at the 2-position. Namely, although the ethyl derivative **1c** gave only **2c** even at ambient temperature, no reaction occurred in 3,3-diphenyl-2-i-propyloxaziridine (**1b**) at benzene refluxing temperature. 2-t-Butyl derivative **1a** gave, contrastly, benzophenone oxime (**3**) and isobutene in almost quantitative yield in the same conditions. This enormous structural dependence is suggestive of some peculiarity of the thermal reaction of **1a**.

First order rate constants and kinetic parameters for the thermal reactions of **1a, b** and **2a, b** at 95 °C were measured by NMR5) (Table 1).6) The reaction of **2a** to **3** is ca. 27 times faster than that of **1a** to **3**. Accordingly, if the reaction follows Boyd's formulation,2) the reaction of **1a** to **2a** is rate-determining. In the isopropyl case **1b**, the thermal reaction gave the corresponding nitrone **2b** at first. This ring opening is much faster than the following reaction, **2b** to **3**. Similarly, if the whole reaction of **1a** follows a successive manner via **2a**, **2a** should be detected during the course of the reaction. We surveyed rigorously by means of HPLC, ^{1}H-NMR, and product isolation. For example, under our reaction condition,7) ca. 5×10^{-3} mol dm^{-3} of the formation of **2a** should be observed at ca. 17 min later by ^{1}H-NMR. No peak for **2a** was observed at all, though this concentration of **2a** is well within a detectable limit of our instrument. As a whole, it is concluded that the thermal reaction of **1a** gave **3** without the intervention of **2a**.

Inspection of kinetic data supports this conclusion. The value for the activation enthalpy of the reaction from **1a** to **3** is 108 kJ mol^{-1} and the estimated activation entropy is -29 J K^{-1} mol^{-1}. According to Grubbs's paper,8) the activation entropy of the thermal decomposition of N-benzhydryl-α,α-diphenylnitrone (**4**), where radical fission and coupling instead of the elimination have occurred, is expected to be moderately large and positive (61 ± 3 J K^{-1} mol^{-1}). By contrast, for a cyclic elimination of the t-butyl group via the five-membered transition state of N-t-butyl-α-phenylnitrone (**5**), a small negative activation entropy (-1 ± 4 J K^{-1} mol^{-1}) is expected. The observed large negative activation entropy is suggestive of the reaction passing through a highly ordered transition state. The substantially lower activation enthalpy for this decomposition9) is also in accord with the expectations based upon the bond energy gain attending the partial carbon-carbon double bond formation.

It is of interest to note that the thermal reactions of **2a, b** showed moderately large positive activation entropies. Comparison of the data with that of **4** and **5** seems to reveal that thermal elimination reactions of **2a, b** tend to give the products via a radical process, instead of the well



a: R = t-Bu
b: R = i-Pr

Table 1. Rate constants and kinetic parameters for the thermal rearrangement of **1** and **2**a)

Reaction	$10^5k/s^{-1}$	$\Delta G^{\ddagger}/kJ\ mol^{-1}$	$\Delta H^{\ddagger}/kJ\ mol^{-1}$	$\Delta S^{\ddagger}/J\ K^{-1}mol^{-1}$
1a → 3	12.2	118	108	-29
2a → 3	332	108	120	33
1b → **2b**	0.44b)	128	99.2	-79 (-8c))
2b → 3	9.9×10^{-4}b)	147	161	38

a) In toluene-d_8 at 95 ± 0.5 °C. b) Rates were measured both in nitrobenzene-d_5 at 150 ± 0.5 °C (**1b** → **2b**) and 190 ± 0.5 °C (**2b** → 3) and the data described are extrapolated values at 95 °C. c) In diphenyl ether.

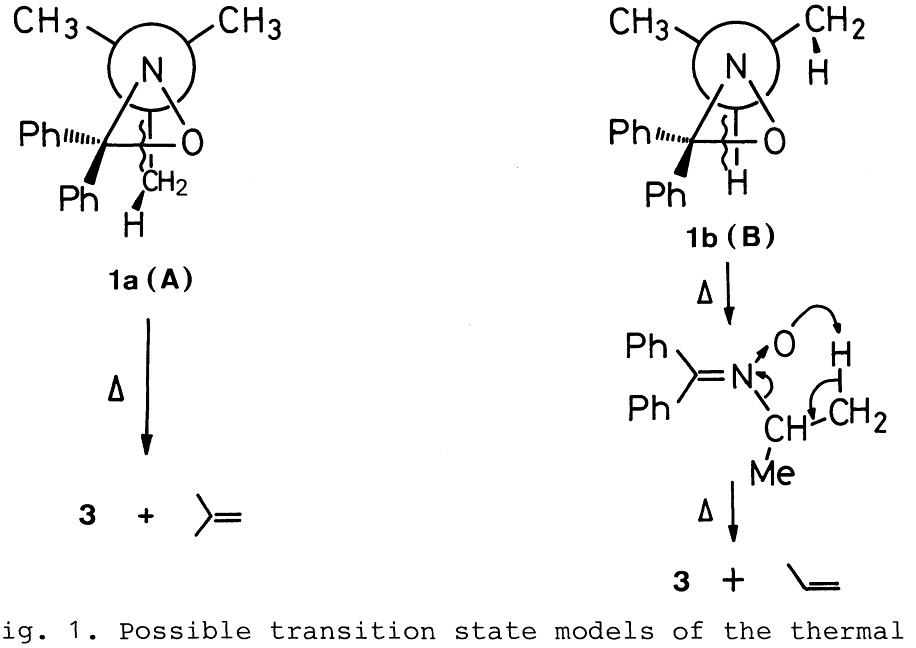


Fig. 1. Possible transition state models of the thermal reactions of the oxaziridines **1a** and **1b**.

established five-membered cyclic transition state of nitrones.10) In addition, a large negative activation entropy of the reaction of **1b** to **2b** may indicate increased solvation of the transition state due to the development of a strong N→O dipole.[11] Measurement of kinetic data in a less polar solvent, diphenyl ether, gave compatibly a small negative activation entropy.

The Newman projection formula of these substrates (**1a** and **1b**) again support the above conclusion (Fig. 1). The stable conformation of **1a** should take the structure **A** to attain the minimum steric repulsion between the methyl and the phenyl groups. As a result, one of the methyl groups is located across the C-O bond of the oxaziridine ring. A hydrogen of the methyl group is very close to the oxygen atom. In the case of **1b**, structure **B** is the stable conformer where the methine proton of the isopropyl group is too far to migrate from there to oxygen. Therefore, it seems reasonable that **1b** gave **2b** at first, followed by a hydrogen migration via a five-membered transition state proposed by Emmons,[2] Boyd,[3] and Grubbs et al.[8]

In summary, while **1b** gave the oxime via the corresponding nitrone, **1a** gave the same product directly. This intramolecular hydrogen migration from the γ-position formally corresponds to the thermal versions of photochemical type II cleavage[12] or the McLafferty rearrangement[13] in mass spectral fragmentations.

References

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5) The rearrangements were followed by ^{1}H-NMR (60 MHz; Hitachi R-24) in toluene-d_8 or nitrobenzene-d_5 solution using the methyl resonance of hexamethylbenzene as internal reference for integration, and linear first order kinetic plots were obtained.
6) For example, first order reaction rates of **1a** to **3** at 80, 95, and 110 ± 0.5 °C were 2.43×10^{-5}, 1.22×10^{-4}, and 4.85×10^{-4} s^{-1}, respectively.
7) Initial [**1a**] was ca. 0.16 mol dm^{-3} in all NMR experiments.
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9) Grubbs et al.[8] reported that E_a of the thermal reactions of **4** and **5** was 171 ± 2 kJ mol^{-1} and 146 ± 1 kJ mol^{-1}, respectively.
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