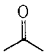
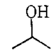
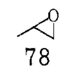
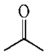
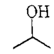
Table III Thermal Decomposition of 1-Chloromercuri-2-hydroxypropane in the Presence of Potassium Alkoxide (ROK) in Alcohol (ROH)

R	ϵ[a]	Products, %			Yields, %	Conversion, %
						
Ethyl[b]	24.3	60	38	2	20	36
n-Butyl	18.2	78	21	1	21	47
sec-Butyl	15.8	87	11	2	83	94

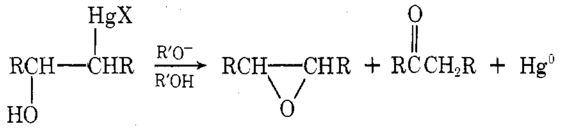
[a] Dielectric constant of the alcohol at 25°. [b] Reaction temperature: refluxing ethanol, 78°.

Table IV Thermal Decomposition of 1-Halomercuri-2-hydroxypropane in the Presence of Potassium *n*-Butoxide in *n*-Butyl Alcohol

Halogen	Registry no.	Products, %			Yields, %	Conversion, %
						
Cl	52358-07-3	78	21	1	21	47
Br	18832-83-2	35	65		14	50
I	5323-64-8	4	96		36	60

clearly indicate two parallel decomposition paths of the intermediate oxymercurial, one leading to the ketone and one to the epoxide.

Nonaqueous Medium. The general procedure consisted of adding to the potassium alkoxide solution the previously prepared halomercurial and heating the resulting mixture.



R′ = H, alkyl

The results given in Table III show that both the yield and the selectivity in epoxide increase with decreasing dielectric constant of the medium. This again points out the dissimilarity with the epoxide formation from chlorohydrins; thus, the formation of an intermediate 1-chloromercuri-2-alkoxide analogous to the 2-chloroethoxide proposed by Swain would be expected to be facilitated in solvents with higher dielectric constants, whereas the opposite was observed.[12]

On the other hand the ease of formation of ketone seems to be influenced by the character of the mercury atom as a leaving group. This was shown by varying the halogen on the oxymercurial. The results are given in Table IV.

The results obtained both in aqueous and nonaqueous medium, although not allowing the establishment of a detailed mechanism, clearly indicate two distinct decomposition paths: one leading to epoxide formation most probably by an intramolecular attack, somehow different from that of 1,2-chlorohydrins, and a second leading to ketone apparently driven by the departure of the mercury atom.

Experimental Section

Materials. All olefins used were commercially available and were used as obtained after verifying their purity by glpc on a 12 m × 6 mm column of 30% dimethylsulfolane on Chromosorb P at 25°. All solvents were purified by distillation following standard methods. Mercuric salts (Prolabo) and alkali metals (Prolabo) were used without further purification.

Oxidation Procedure. The general procedure was discussed in the text. All product analyses were carried out by glpc using tetrahydrofuran as an internal standard. Products were identified by spectroscopic methods on preparative glpc purified samples and compared with authentic samples.

Aqueous Medium. A suspension of 80 mmol of mercuric salt in 150 ml of water was placed under an atmosphere of gaseous olefin. In the case of liquid olefins, the stoichiometric amount of substrate was added to the aqueous suspension and stirring continued for 1 hr. The resulting solution was then placed in the reaction vessel equipped with a gas inlet tube, a mechanical stirrer, and a reflux condenser kept at 60–65°. The mixture was rendered basic (pH 13) by slowly adding 14 g of potassium hydroxide and then heated to 100° for 6 hr. The products formed were swept out by a continuous flow of nitrogen gas (5 l./hr) and collected in two flasks placed in series and cooled to −45°. After cooling the reaction mixture, hydrochloric acid was added and the amount of olefin regenerated was measured.

Nonaqueous Medium. To the desired potassium alkoxide (80 mmol) in 100 ml of alcohol, placed in the reaction vessel described for the aqueous reaction, was added a 100-ml alcoholic solution containing 80 mmol of the previously prepared 1-halo-2-hydroxypropane. Heating the mixture for 6 hr at 82° while nitrogen gas swept the system gave the reaction products which were collected and analyzed in a manner analogous to the reaction in water.

Preparation of 1-Halomercuri-2-hydroxypropane. The procedure followed was the one described by Hofmann and Sand.[13] A 300-ml aqueous solution containing 200 g (0.63 mol) of mercuric acetate was placed under an atmosphere of propene. Vigorous agitation resulted in the absorption of 13.24 l. of gas. The solution obtained was neutralized by adding slowly 40 g (0.7 mol) of potassium hydroxide dissolved in 100 ml of water, adjusted to neutrality with CO_2 and then divided into three aliquots. Each part was then treated separately with 0.21 mmol of sodium chloride, bromide, and iodide to give white precipitates which were filtered and recrystallized from diethyl ether. The products obtained were respectively: 1-chloromercuri-2-hydroxypropane (42 g, 68% yield), mp 51° (lit.[13] 53°); 1-bromomercuri-2-hydroxypropane (54 g, 75% yield), mp 78° (lit.[13] 76°); and 1-iodomercuri-2-hydroxypropane (40 g, 50% yield), mp 65° (lit.[13] 68°). All solids were stored under nitrogen and in the dark before use.

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A Kinetic Study of the Thermal Decomposition of (*Z*)-*N*-*tert*-Butyl-α-phenylnitrone[1,2]

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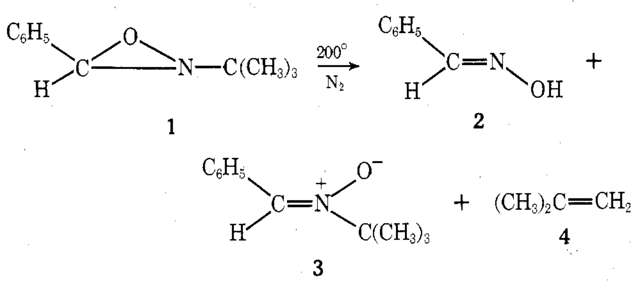
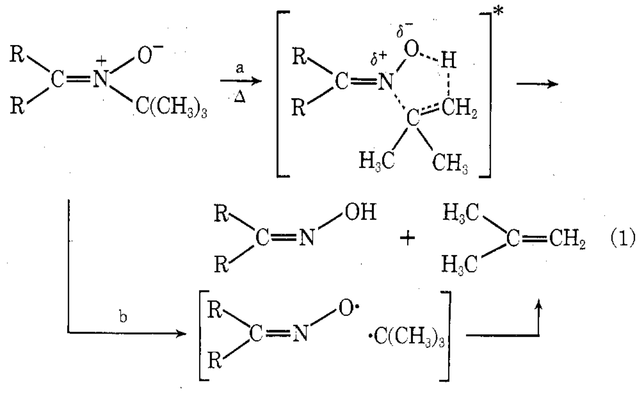
Received June 10, 1974

The vapor-phase pyrolysis of 2-*tert*-butyl-3-phenyloxaziridine (1) was described by Emmons in 1957.[3] The products were reported to be benzaldoxime (**2**), *N*-*tert*-butyl-α-phenylnitrone (**3**), and isobutylene (**4**) contaminated with small amounts of *tert*-nitrosobutane, nitrous oxide, and carbon dioxide. A concerted cyclic elimination from the initially formed nitrone was suggested as the probable mechanism for the formation of the oxime and olefin. Such cyclic eliminations are well documented for tertiary amine oxides bearing β-hydrogens. Recently Boyd[4] showed that the thermal elimination of olefins from various *N*-alkylnitrones is quite general.



Although a concerted decomposition (illustrated in route a for an *N*-*tert*-butylnitrone) seems reasonable, a homolytic dissociation followed by disproportionation (route b) warrants consideration.[5] We have recently shown that a homolytic cleavage of the C–N bond is the principal mode of decomposition of *N*-benzhydryl-α,α-diarylnitrones.[6,7]



A kinetic comparison of the thermolyses of **3** and *N*-benzhydryl-α,α-diphenylnitrone (**5**) in *tert*-butyl alcohol appeared to offer a useful mechanistic probe. The entropy of activation for the decomposition of **5**, which clearly involves the formation of iminoxy and benzhydryl radicals, was expected to be moderately large and positive. In diethylcarbitol this was found to be 11 eu.[8] By contrast, for a cyclic elimination (from **3**) a modest negative ΔS^* might reasonably be expected. Entropies of activation for thermolyses of neutral compounds, transition states for which involve five- or six-membered structures, fall in the range of -2 to -17 eu.[9] Useful comparison examples are the thermal decompositions of *erythro*- and *threo*-*N*,*N*-dimethyl-3-phenyl-2-butylamine oxides in aprotic solvents which exhibit entropies of activation ranging from $+0.6$ (± 2.1) to -10.5 (± 2.5) eu.[10]

Rate constants for the thermal decompositions of **3** and **5** in *tert*-butyl alcohol obtained in the present study are listed in Table I. The activation parameters calculated from the data in Table I are for **3**, $E_a = 34.9 \pm 0.3$ kcal/mol; $\Delta S^* = -0.3 \pm 0.9$ eu; for **5**, $E_a = 40.9 \pm 0.4$ kcal/mol; $\Delta S^* = +14.5 \pm 0.8$ eu. The *N*-benzhydrylnitrone (**5**) leads to the formation of *O*-benzhydrylbenzophenone oxime in nearly quantitative yield by recombination of iminoxy and benzyhydryl radicals. From the decomposition of **3**, benzaldoxime was produced in 97% yield as determined by ultraviolet spectroscopy and isobutylene was isolated in 90% yield. The near zero value of ΔS * for the decomposition of **3** is consistent with a cyclic transition state but not in accord with expectations if homolytic dissociation or ion pair formation were involved. The substantially lower activation energy for this decomposition (compared with that of **5**) is also in accord with expectations based upon the bond energy gain attending partial carbon-carbon double bond formation. The high yield of oxime and olefin renders unlikely and significant cycloaddition of isobutylene with unreacted nitrone.

Table I
First-Order Rate Constants[a] for the Thermal Decompositions of *N*-*tert*-Butyl-α-phenylnitrone (3) and *N*-Benzhydryl-α,α-diphenylnitrone (5) in *tert*-Butyl Alcohol

Nitrone	Concn, m*M*	Temp, °C	$10^5 k$, sec^{-1}
3	2.53	135	0.368
3	2.63	135	0.385
3	0.229	150	1.86
3	1.20	150	1.70
3	1.20	150	1.88
3	2.44	150	1.76
3	1.03	165	7.09
3	2.62	165	7.39
5	3.44	130	0.250
5	0.733	130	0.232
5	0.745	130	0.236
5	2.41	144	1.26
5	3.50	144	1.28
5	2.58	144	1.32
5	0.906	144	1.30
5	0.664	144	1.34
5	0.596	144	1.35
5	3.07	160	7.66
5	2.84	160	7.97
5	0.930	160	8.13
5	0.650	160	8.22

[a] The average probable error on individually determined rate constants was ±1%.

Experimental Section[13]

***N*-Benzyl-*tert*-butylimine** was prepared according to the procedure of Emling and coworkers[14] in 83% yield: bp 77.5–79° (4 mm), n^{25}D 1.5212, ir (neat) 1650 cm^{-1} (C=N).

2-*tert*-Butyl-3-phenyloxaziridine (1) was prepared by *m*-chloroperbenzoic acid oxidation of the above imine using the procedure described by Pews.[15] The unpurified product (96% yield) was obtained as a pale yellow oil: pmr (CCl$_4$) δ 7.4–7.2 (m, 5, aromatic), 4.50 (s, 1, α C–H), 1.15 (s, 9, C(CH$_3$)$_3$).

***N*-*tert*-Butyl-α-phenylnitrone (3)** was prepared by the thermal isomerization of **1** in acetonitrile as described by Emmons.[3] The nitrone was recrystallized from 10% ether-petroleum ether (bp 90–110°) followed by recrystallization from 20% ether–hexane. The product used was a colorless crystalline material: mp 73.5–74.5° (lit.[3] mp 75–76°); pmr (CCl$_4$) δ 8.25–8.02 (m, 2, aromatic), 7.38–7.15 (m, 4, aromatic + vinyl protons), 1.53 (s, 9, C(CH$_3$)$_3$); uv (C$_2$H$_5$OH) λ_{max} 293.5 nm (ϵ, 17,700), 224 nm (ϵ, 7,240).

***N*-Benzhydryl-α,α-diphenylnitrone (5)** was prepared as previously described.[16]

General Procedures for the Kinetic Runs. A solution of the nitrone was prepared with *tert*-butyl alcohol which had been dried over CaO and distilled from Dri-Na under nitrogen. Approximately 1 ml of the solution was pipetted into each of 5-10-ml Pyrex tubes. These solutions were then degassed and sealed under vacuum. For a given run the tubes were simultaneously placed in a constant temperature oil bath (±0.05°). Tubes were removed periodically and quenched at low temperature. Infinity tubes remained in the bath for 10 half-lives. The opened tubes were allowed to warm to room temperature in a desiccator. Aliquots were weighed by difference into volumetric flasks and diluted with absolute ethanol. Rate constants were determined for the disappearance of the nitrone by following the decrease in its absorption at 293.5 (for **3**) and 310 nm (for **5**).

Product Analyses. Small samples of **5** were decomposed (99.9% reaction based upon rates) in *tert*-butyl alcohol at 144°. After removal of solvent under reduced pressure, the residue was carefully chromatographed over alumina. Hexane-benzene (49:1) mixtures eluted approximately 1-2% tetraphenylethane. Hexane–benzene (4:1) eluted *O*-benzhydrylbenzophenone oxime in yields as high as 96%.

The yield of benzaldoxime from the decomposition of **3** in *tert*-butyl alcohol (measured by ultraviolet spectroscopy) was 97%. The opened reaction ampoules were then attached to a vacuum line, and the isobutylene was distilled from the solution and collected under reduced pressure. The isobutylene (90% determined volumetrically) was identified by infrared and mass spectra.

Acknowledgment. The authors wish to thank Dr. Morey Ring for his assistance in isolating the isobutylene using vacuum line techniques.

Registry No.—**1,** 7731-34-2; **3,** 52392-70-8; **5,** 5350-59-4; *N*-benzyl-*tert*-butylimine, 6852-58-0.

References and Notes

(1) This work was supported in part by the National Science Foundation in a grant (GY-9550) to M.H.G. for an Academic Year Extension of Research Participation for College Teachers.

(2) The rate data for the thermal decomposition of *N*-benzhydryl-α,α-diphenylnitrone (also described in this note) were taken from the Ph.D. thesis of J. A. Villarreal. This part of the study was supported by the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA-10741-04).

(3) W. D. Emmons, *J. Amer. Chem. Soc.*, **79,** 5739 (1957).

(4) D. R. Boyd, *Tetrahedron Lett.*, 3467 (1973).

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(7) With these nitrones no β C–H bond is available for a cyclic elimination, and the two aromatic rings are effective in stabilizing the alkyl radical being formed in the rate-determining step.

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(9) C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.*, **82,** 1810 (1960).

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Thermolysis of Heterocyclic Azides. Rearrangement Involving Acyl Migration from Carbon to Nitrogen

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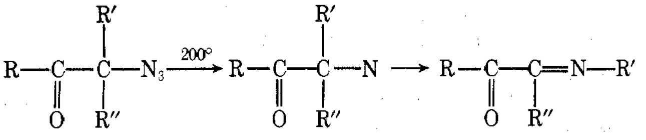
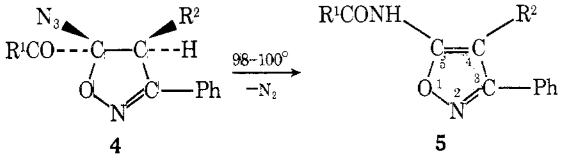
Received May 23, 1974

Boyer and Straw have shown that aliphatic α-azidocarbonyl compounds (**1**) decompose at 200 ± 20° to give imines (**3**), probably *via* the intermediacy of nitrenes (**2**).[1] In



1 2 3

this reaction migration of hydrogen, methyl, or phenyl occurred and no acyl migration was observed. We now want to report two examples of acyl migration from carbon to nitrogen when R′ and R″ are part of a heterocyclic ring such as in eq 1.[2]

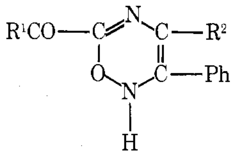


(1)

4 5

a, R^1 = Me; R^2 = Ph
b, R^1 = Ph; R^2 = Me

The 5-azido-5-acylisoxazolines **4a** and **4b** used in this work were obtained, among other products, from the reactions of α-azidovinyl ketones with benzonitrile oxide.[3] Thermolysis of **4a,b** in toluene at *ca.* 100° resulted in evolution of nitrogen and formation of white crystals which exhibited microanalyses and spectral data consistent with structure **5a,b.** The alternative structures **6** and **7,** which



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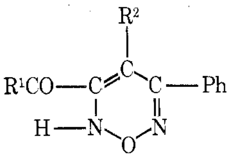

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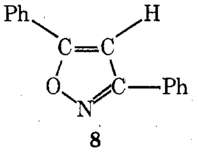
would result from **4** by loss of nitrogen and ring expansion, are easily excluded by the absence of a ketone C-atom absorption at about 190–200 ppm in the ^{13}C nmr spectra.

The chemical shift data of compounds **4a** and **4b** are summarized in Table I. Assignment of the ring carbon absorptions was based on comparison with the model compounds **8** and **9.**[3] These compounds possess CH ring C

Table I
^{13}C Chemical Shifts with Respect to TMS (DMSO-d_6 as Solvent)

Compd	C$_3$	C$_4$	C$_5$
5a[a]	162.4	110	159.1
5b[b]	163.6	103.8	159.5
8	164	97.5	170.5
9	161.6	119.3	163.6
11	161.7	91.4	167.7

[a] For this compound the CH$_3$CO carbon atoms absorb at δ 22.6 and 170. Compare these values with δ 24.1 and 169.5 for the acetyl group in acetanilide: L. F. Johnson and W. C. Jankowski, "Carbon-13 Nmr Spectra. A Collection of Assigned, Coded, and Indexed Spectra," Wiley-Interscience, New York, N.Y., 1972, Spectrum no. 295. [b] For this compound the CH$_3$ and C=O carbon atoms absorb at δ 8 and 165.6.



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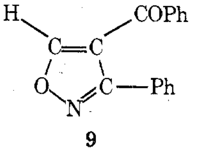

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atoms whose position in the nmr spectra can be determined by the off-resonance spin-decoupling technique. The values reported in Table I are consistent with expectation. Indeed,