

TABLE I
 THERMAL DECOMPOSITION PRODUCTS OF DIALKYL PEROXIDES

Peroxide	Temp, °C	Products	Mole/100 mol of ^a <i>t</i> -alkoxy radical
<i>t</i> -Butyl peroxide ^b (I)	110	<i>t</i> -Butyl alcohol	24.8
		Acetone	32.8
		Isobutylene oxide (II)	34.9
<i>t</i> -Amyl peroxide (III)	115	<i>t</i> -Amyl alcohol	8.5
		Acetone	83.0
		2-Butanone	2.0
		1,1,2-Trimethylethylene oxide (IV)	5.0
		1-Ethyl-1-methylethylene oxide (V)	1.1

^a Based on moles of peroxide decomposed. ^b Data from ref 2.

at 115° indicate, however, that only a small amount of 1,1,2-trimethylethylene oxide (IV) is formed. The rate of decomposition of III in the liquid state is, however, faster than either in the gas phase or in solvents (Table II) that do not produce radicals that induce the decomposition of dialkyl peroxides.³

 TABLE II
 DECOMPOSITION RATE OF *t*-AMYL PEROXIDE (III)

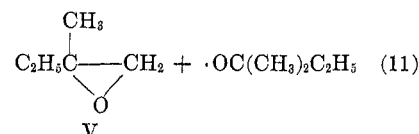
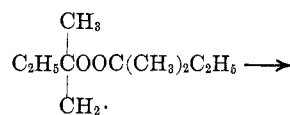
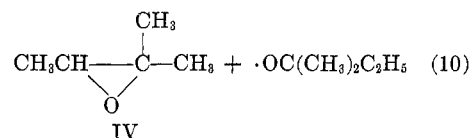
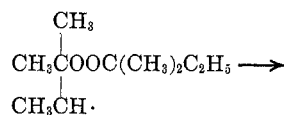
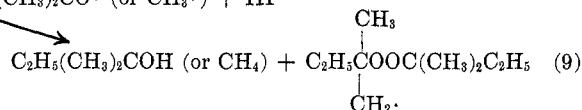
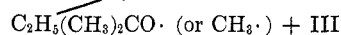
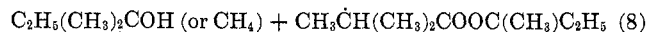
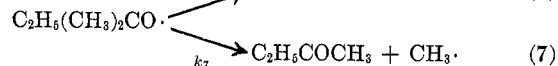
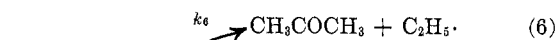
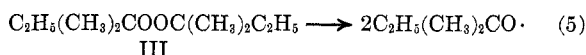
Solvent ^a	Temp, °C	$k \times 10^4 \text{ sec}^{-1}$	Half-life, min
Gas phase	132.2	0.72 ^b	
Neat	132.2	(1.15) ^c	100.4
Gas phase	125.0	0.27 ^d	427.7
Neat	125.0	(0.57) ^c	200.8
<i>trans</i> -Decalin	125.0	0.28	402.4
<i>cis</i> -Decalin	125.0	0.28	408.0
Triethylamine	125.0	0.35	323.0
Cyclohexane	125.0	0.36	313.0
Cyclooctane	125.0	0.29	386.0
Octane	125.0	0.30	381.0

^a Mole ratio of solvent to peroxide is 5:1. ^b Reference 2. ^c First-order kinetics observed through first half-life of the decomposition. ^d Extrapolated from data in ref 2.

Hydrogen abstraction from *t*-butyl peroxide to yield the precursor of isobutylene oxide is performed, for the most part, by the *t*-butoxy radical, a species reactive enough to abstract the primary alkyl hydrogens of I. Some of the hydrogen abstraction from I (~30%) is performed by methyl radicals which are also reactive hydrogen abstractors. Methyl radicals are formed in the fragmentation reaction of the *t*-butoxy radical (reaction 2), a reaction which competes favorably, but not to the exclusion of, hydrogen abstraction from I by the *t*-butoxy radical.

The small amount of *t*-amyl alcohol formed in the reaction of III indicates that fragmentation of the *t*-amyloxy radical is faster than hydrogen abstraction from the alkyl portion of III by the radical. Furthermore, elimination of an ethyl radical occurs more readily than elimination of a methyl radical ($k_6/k_7 = 20.8$)⁴ as evidenced by the amount of acetone formed relative to 2-butanone. The small amounts of 1,1,2-trimethylethylene oxide (IV) and 1-ethyl-1-methylethylene oxide (V) formed in the chain sequence 9 and 11 indicate that hydrogen abstraction from the alkyl portion of the peroxide does not occur readily. Apparently the hydrogen atom abstraction is performed only by the reactive *t*-amyloxy and methyl radicals, both of which are present in small amounts owing to the rapid fragmenta-

tion of alkoxy radicals yielding mainly ethyl radicals. The ratio of attack of the secondary with respect to the primary hydrogens of III, calculated from the relative amounts of IV and V, is 4.5 indicating a reactivity ratio of secondary to primary hydrogens of 13.5. Abstraction of hydrogen atoms apparently is performed by reactive free radicals (or radical) that do not discriminate greatly between primary and secondary hydrogens. Both alkoxy and methyl radicals would be expected to be less selective in hydrogen abstraction reactions than the energetically more stable ethyl radicals which likely couple or disproportionate in these reactions.



Our work does not explain the enhanced rate of decomposition of III in the liquid phase. It does suggest, however, that it is not the result of extensive attack at the alkyl portion of the peroxide as in the *t*-butyl peroxide reactions. The observation that the decomposition rate increases with increasing pressure in the gas phase² may be indicative of a mechanism for the reac-

(3) E. S. Huyser and C. J. Bredeweg, *J. Amer. Chem. Soc.*, **86**, 2401 (1964); E. S. Huyser, C. J. Bredeweg, and R. M. VanScoy, *ibid.*, **86**, 4148 (1964).

(4) See J. K. Kochi, *ibid.*, **84**, 1193 (1962).

tion more complex than the assumed unimolecular decomposition of this dialkyl peroxide.

Experimental Section

Materials.—*t*-Amyl peroxide was prepared by the method described by Milas and Surgenor.⁵ The crude peroxide was distilled twice [bp 44–45° (10 mm)] through a 40-mm glass bead column and yielded a sample at least 98% pure by gas chromatographic analysis. Authentic samples of 1,1,2-trimethylethylene oxide (IV) and 1-ethyl-1-methylethylene oxide (V) for gas chromatographic analysis were prepared from the appropriate alkenes by reaction with peracetic acid as described by Sorenson and Campbell.⁶ The nmr spectrum of 1,1,2-trimethylethylene oxide (bp 74–74°) showed a multiplet at 1.2 ppm and a quartet at 2.7 ppm in a ratio of 10:1. The 1-ethyl-1-methylethylene oxide (bp 80–81°) has an nmr spectra with a triplet at 0.9 ppm, a singlet at 1.2 ppm, a quartet at 1.5 ppm, and a singlet at 2.4 ppm.

Rate Determinations.—Samples approximately 1 ml in size of either the pure peroxide or solution were placed in several 9 mm × 9 in. Pyrex tubes. After sparging with nitrogen and cooling, the tubes were sealed and placed in a constant-temperature oil bath at the temperature indicated in Table II. The tubes were withdrawn at various time intervals; the amount of peroxide remaining was determined by gas chromatographic analysis of the contents of the tubes employing the method described previously for determination of *t*-butyl peroxide.³

Thermal Decomposition of Liquid *t*-Amyl Peroxide.—A small amount of peroxide was placed in a glass tube, sealed, and heated for 17 hr at 115°. A portion of the resulting mixture was subjected to gas chromatographic analysis on two different columns (0.25 in. × 13 ft column packed with 17% dodecyl phthalate on Chromosorb W and 1/8 in. × 19 ft column packed with 20% TCEP on Chromosorb W). The products of the reaction were identified by comparison of their retention times on both columns with authentic samples of the materials. The quantities were determined from the peak areas of each component as measured with a Disc Integrator. No attempt was made to analyze the gaseous products of the reaction.

Registry No.—III, 10508-09-5.

- (5) N. A. Milas and D. N. Surgenor, *J. Amer. Chem. Soc.*, **68**, 643, (1946).
 (6) W. R. Sorenson and T. W. Campbell, "Preparative Methods of Polymer Chemistry," 2nd ed, Interscience, New York, N. Y., 1968, p 370.

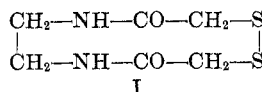
A Ten-Membered-Ring Cyclic Disulfide¹

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Reaction of ethylenediamine with methyl or butyl dithiodiglycollate in the absence of solvent affords the cyclic disulfide diamide N,N'-ethylenedithiodiglycollamide (perhydro-1,2,5,8-dithiadiazecine-4,9-dione, I) in excellent yield. The same product, rather than the



expected low polymer with amine end groups, results in fair yield even from reaction of the ester with a considerable excess (up to 1.6 mol) of the amine. Poorer yields result from reaction in solution in ethanol or dimethylformamide. The disulfide is quite stable at

(1) Financial support from the National Institute of General Medical Sciences, Public Health Service, Research Grant GM 16477, is gratefully acknowledged.

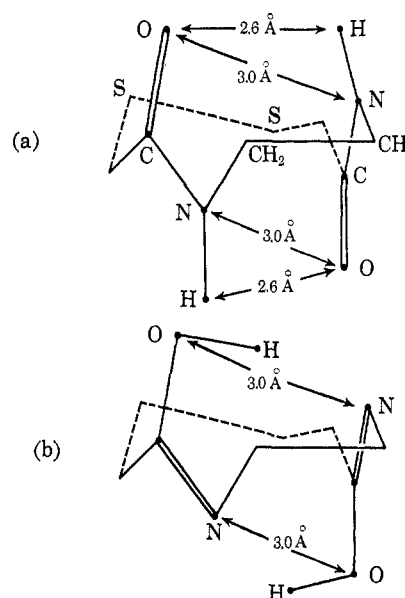


Figure 1.—Skeletal structures for N,N'-ethylenedithiodiglycollamide: (a) amide extreme, (b) isoamide extreme.

room temperature but undergoes some decomposition upon heating, in solution in dimethylformamide, and at temperatures above 100°.

The monomer structure, I, is indicated by the mass spectrum and elemental analysis. Chromatographic homogeneity and the expected retardation are observed upon gel filtration (Sephadex G 10 or G 15); by which means the material is readily separated from a putative dimer² which results from it upon exposure, in aqueous solution, to X-rays.

Such ready formation of a ten-membered ring is unusual.³ Several contributing restrictions are apparent, however. Substantial hindrance to free rotation about the disulfide bond⁴ and the necessary planarity of the amide group in the presumptive monoamide intermediate (NH₂CH₂CH₂NHCOCH₂SSCH₂COOR) restrict the conformations which this may adopt essentially to those available to apodeictically cyclizable six-centered systems such as δ -aminovaleric acid. The cyclic product can adopt a strain-free and uncrowded, though compact, conformation (Figure 1) in which all six centers of each amide unit are coplanar, the preferred (10–15 kcal mol⁻¹)⁴ dihedral angle of $\sim 90^\circ$ about the disulfide group is maintained and, indeed, even the diamidoethane moiety has the *gauche* conformation. It is noteworthy that the length of the disulfide bond (2.04 Å) contributes significantly to the lack of both crowding and strain. The internuclear distance between each carbonyl oxygen and the juxtaposed nitrogen of the antipodal amide group is 2.9–3.0 Å, approximately the sum of the respective van der Waals' radii. The probability of duple, strong intramolecular hydrogen bonding seems considerable. The formal

(2) T. C. Owen and A. C. Wilbraham, *J. Amer. Chem. Soc.*, **91**, 3365 (1969).

(3) H. Stetter and J. Marx, *Justus Liebigs Ann. Chem.*, **607**, 59 (1957), have prepared a number of simple macrocyclic diamides. The yields of larger rings (12 centers and above) were good but the 10-membered rings, ethylene-adipamide and tetramethylenesuccinamide, were obtained only in yields of 24 and 34%, respectively, even under high-dilution conditions and with carefully purified reactants.

(4) O. Foss, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961.