afford 3.83 g. of a white solid, m.p. 125–190°. Repeated recrystallization of this material and chromatography of the mother liquors on alumina and silica gel afforded 1.24 g. (76% yield) of tetraphenylethylene, m.p. and m.m.p. 223–224°; 220 mg. of dibenzhydryl ether, m.p. 100–103°, identified by mixed melting point and infrared; and 2.12 g. (93% yield) of triphenylcarbinol, m.p. 155–158°, m.m.p. 158–160°.

Catalytic Dimerization of Diphenyldiazomethane.—A solution of 12.5 g. (64.5 mmoles) of diphenyldiazomethane (m.p. 29°) in 100 ml. of dry ether was added over a 10-min. period to a stirred slurry of 1.15 g. (3.35 mmoles) of trityl perchlorate in 100 ml. of ether at 0°. The purple color was discharged rapidly on addition. After stirring at 0° for an additional 10 min., saturated sodium bicarbonate solution was added, the ether layer was separated, and the aqueous layer was extracted with benzene. The combined organic layers were washed with saturated salt solution, dried over anhydrous sodium sulfate and evaporated. Repeated recrystallization of the residue and chromatography of the mother liquors on alumina and silica gel afforded 10.36 g. (97% yield) of tetraphenylethylene, identified by m.p., m.m.p., and infrared; 932 mg. (96% yield) of triphenylcarbinol, m.p. and m.m.p. 160.5–161.5°; and 206 mg. (1.8% yield) of dibenzhydryl ether as needles, m.p. 105–107.5°, m.m.p. 107–108°.

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.11; H, 6.33. Found: C, 88.98, 88.89; H, 6.35, 6.38.

Hydrolysis of a 135-mg. sample of the dibenzhydryl ether in refluxing aqueous dioxane–sulfuric acid for 12 hr. gave, on chromatography, 32 mg. of recovered ether and 95 mg. (89% yield) of benzhydrol, m.p. 64.5–65.5°, m.m.p. 65.5–66.0°.

Tetra-(*p*-anisyl)-ethylene.—A solution of 2.56 g. (10.1 mmoles) of di-(*p*-anisyl)-diazomethane[29] (m.p. 110°) in 100 ml. of dry ether was added dropwise to a stirred slurry of 273 mg. (0.80 mmole) of trityl perchlorate in 25 ml. of dry ether at 0°. A rapid evolution of nitrogen accompanied by discharge of the blue-purple color of the diazo compound occurred. After completion of addition of the diazo compound the unreacted trityl perchlorate was hydrolyzed by the addition of saturated sodium bicarbonate solution. The ether layer was separated and the aqueous layer was extracted with benzene. The combined organic layers were washed with saturated salt solution, dried over anhydrous sodium sulfate and evaporated. One crystallization of the white residue from ethyl acetate gave 1.91 g. (84% yield) of tetra-(*p*-anisyl)-ethylene as rods, m.p. 184–185° (lit.[30] m.p. 181–182°).

Anal. Calcd. for $C_{36}H_{28}O_4$: C, 79.62; H, 6.24. Found: C, 79.93; H, 5.95.

Boron Trifluoride Etherate and Diphenyldiazomethane.—To a solution of 1.080 g. (5.56 mmoles) of diphenyldiazomethane (m.p. 29°) in 10 ml. of dry ether was added at 0° 1 drop of freshly distilled boron trifluoride etherate. Nitrogen was vigorously evolved. After standing at 0° for 0.5 hr. the solution was a pale yellow color, a white precipitate had appeared, and nitrogen evolution had ceased. Evaporation of the solvent afforded 992 mg. (99% yield) of slightly yellow rods, m.p. 150–160°. Percolation of a hexane solution of this material through a column of alumina afforded 911 mg. (91% yield) of benzophenone azine as pale yellow rods, m.p. 162–163° (lit.[31] m.p. 164°). The analytical sample was prepared by recrystallization from ethyl acetate as pale yellow rods, m.p. 163°.

Anal. Calcd. for $C_{26}H_{20}N_2$: C, 86.63; H, 5.59; N, 7.77. Found: C, 86.52; H, 5.59; N, 7.71.

Aluminum Chloride and Diphenyldiazomethane.—To a solution of 1.155 g. (5.95 mmoles) of diphenyldiazomethane (m.p. 29°) in 10 ml. of dry ether was added a solution of 55 mg. of freshly sublimed aluminum chloride in 1 ml. of ether. After being stirred at 25° for 8 hr. the now colorless solution was taken up in benzene, washed with saturated sodium bicarbonate solution and saturated salt solution, dried over anhydrous sodium sulfate and evaporated. The residue, 1.023 g. of yellow crystals, m.p. 140–190°, was chromatographed on silica gel (100 g.). Elution with 25% chloroform in hexane afforded directly 464 mg. (47% yield) of tetraphenylethylene, m.p. and m.m.p. 224–224.5°. Elution with 40% chloroform in hexane afforded 577 mg. (54% yield) of benzophenone azine, m.p. 161.5–163°. One recrystallization from ethyl acetate gave 414 mg. (38% yield) of rods, m.p. 163°, m.m.p. 162.5–163°.

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[29] R. Baltzly, N. B. Mehta, P. B. Russell, R. E. Brooks, E. M. Grivsky and A. M. Steinberg, *J. Org. Chem.*, **26**, 3669 (1961).

[30] L. Gattermann, *Ber.*, **28**, 2874 (1895).

[31] A. Purgotti and G. Vigand, *Gazz. chim. ital.*, **31**, **II**, 560 (1902).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY, STANFORD, CALIF.]

Peroxides. X. The Thermal Decomposition of 1-Hydroxyisobutyl-1-*d* Isobutyl-1,1-d_2 Peroxide and Related Compounds[1]

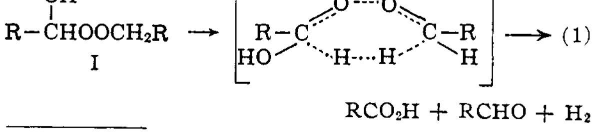
BY LOIS J. DURHAM AND HARRY S. MOSHER

RECEIVED DECEMBER 18, 1961

A kinetic study has been made of the thermal decomposition reaction of 1-hydroxyisobutyl-1-*d* isobutyl-1,1-d_2 peroxide and related deuterium labeled compounds, which yield acid, aldehyde and isotopic hydrogen. A minimum isotope effect [k_H/k_D] of between three and four was observed and has been interpreted as evidence for the proposed cyclic concerted mechanism. The introduction of deuterium into this peroxide has reduced the rate of the hydrogen evolution reaction to such an extent that competing side reactions now account for the major portion of the decomposition. For this reason strict quantitative interpretation of the results was not possible although approximate values for the enthalpy and entropy of activation have been reported for the reaction involving the evolution of deuterium from the trideuterated peroxide.

Introduction

Previous research on the thermal decomposition of primary 1-hydroxyalkyl alkyl peroxides involving product analysis[2] and kinetic studies[1] gave evidence which was interpreted in terms of a cyclic concerted mechanism (eq. 1) to explain the formation of acid, aldehyde and molecular hydrogen. The possibility of this reaction also being explained by a cage mechanism led to the present investigation. Presumably a radical cage-type mechanism would involve as a first step the homolytic cleavage of the O–O bond. Once formed, the radical fragments would be in a position to react either with each other or with solvent molecules within the solvent cage. From the principles of primary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(1)

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[1] Paper IX in this series, L. J. Durham and H. S. Mosher, *J. Am. Chem. Soc.*, **82**, 4537 (1960).

[2] L. J. Durham, C. F. Wurster and H. S. Mosher, *J. Am. Chem. Soc.*, **80**, 332 (1958).

recombination of radicals,[3,4] it would be expected that the rate of interaction between the newly formed radicals would exceed the rate of reaction with solvent. In a study employing independent runs of isotopically pure species, if the rate of reaction of these radicals with each other to produce hydrogen greatly exceeded their rate of generation by the prior O–O bond cleavage, little or no effect would be observed on the rate of hydrogen evolution *versus* the rate of deuterium evolution by virtue of the substitution of deuterium for hydrogen in the α-positions of the peroxide I.

If the less likely assumption is made that the rate-determining step in the cage mechanism is the recombination of the radicals, then a kinetic isotope effect would also be anticipated. However, the necessity of considering this alternative is obviated by the prior observation[1] of a negative entropy of activation for the reaction which seems incompatible with the radical recombination step being rate determining. The determination of the isotope effect therefore appears to be a critical test for the mechanism of this reaction.

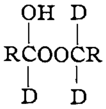
Experimental

Preparation of Deuterated Compound.—Isobutyl-1,1-d_2 alcohol was prepared by the method of Streitwieser and Schaeffer[5] by reducing *n*-octyl isobutyrate with acetic acid-*d* and sodium, except that a dispersion of sodium metal in *o*-xylene was used instead of pieces of sodium in ether solvent. In the work-up of the reaction mixture *o*-xylene was used rather than ether. Fractional distillation of the dried *o*-xylene solution yielded not only the desired isobutyl-1,1-d_2 alcohol (about 40% yield) but also a small amount of isobutyraldehyde-1-*d* (about 3% yield). These products were contaminated by varying amounts of solvent, but since *o*-xylene did not interfere with subsequent reactions no attempt was made to remove it at this stage.

Mass spectrographic analysis[6] of a sample of the isobutyraldehyde-1-*d*, purified by gas chromatography, indicated almost complete deuteration on the aldehyde carbon atom and also about *35% deuteration on the α-carbon atom as well.* This could be deduced from the 73 and 74 *m/e* peaks as well as the 43 and 44 *m/e* peaks as compared to the mass spectrum of the undeuterated aldehyde. Analysis by integration of the n.m.r. spectrum[7] was more accurate and indicated 96.0 ± 0.3% deuterium on the aldehyde carbon and 32 ± 1% deuteration on the α-carbon atom. The isobutyl-1,1-d_2 alcohol was found to be 94.9 ± 0.1% deuterated on the alcohol carbon (5.1 ± 0.1% proton on the alcohol carbon) by n.m.r. analysis and practically free of deuteration in the α-position. This analysis was confirmed by the mass spectrum which had a molecular ion peak at 76 *m/e* and only a trace peak at 77 *m/e*.[8]

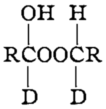
Isobutyl-1,1-d_2 hydroperoxide was prepared from the deuterated alcohol *via* the methanesulfonate in the same manner as used for the undeuterated material.[9]

1-Hydroxyisobutyl-1-*d* isobutyl-1,1-d_2 peroxide was prepared from the corresponding deuterated aldehyde and hydroperoxide with the above deuterium composition in the same manner as for undeuterated material.[1] The partially deuterated 1-hydroxyisobutyl isobutyl-1,1-d_2 and 1-hydroxyisobutyl-1-*d* isobutyl peroxides were prepared in the same manner starting with the appropriate deuterated or undeuterated aldehyde and hydroperoxide. Since there are six possible arrangements of hydrogen and deuterium in the α-position of I, namely I–VI, and the starting materials were not isotopically pure, each of these products A, B and C, represents a mixture with the major component[10] corresponding, respectively, to II, V and IV.



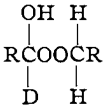
$$\mathrm{R\overset{OH}{\underset{D}{C}}OO\overset{D}{\underset{D}{C}}R}$$

II



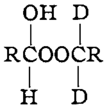
$$\mathrm{R\overset{OH}{\underset{D}{C}}OO\overset{H}{\underset{D}{C}}R}$$

III



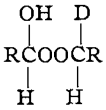
$$\mathrm{R\overset{OH}{\underset{D}{C}}OO\overset{H}{\underset{H}{C}}R}$$

IV



$$\mathrm{R\overset{OH}{\underset{H}{C}}OO\overset{D}{\underset{D}{C}}R}$$

V



$$\mathrm{R\overset{OH}{\underset{H}{C}}OO\overset{D}{\underset{H}{C}}R}$$

VI

Decomposition of Deuterated Compounds.—The apparatus and techniques used in the kinetic studies have already been described.[1] The decomposition data are summarized in Table I.

TABLE I

DECOMPOSITIONS OF DEUTERIUM LABELED I IN α-METHYLSTYRENE

Temp.,[a] °C.	Initial concn., *m*	Sample, wt., mg.	H_2, % Purity[b]	H_2, % Yield[c]	$T_{1/2}$,[d] sec.
(A) 1-Hydroxyisobutyl-1-*d* isobutyl-1,1-d_2 peroxide (II)					
99.6	0.452	216	..	38	7100
109.8	.473	390	85	27	3100
110.0	.468	541	73–91[f]	20–25[f]	3600
122.0	.467	284	..	<30	1600
(B) 1-Hydroxyisobutyl isobutyl-1,1-d_2 peroxide (V)					
109.6	0.480	517	91	23	2100
(C) 1-Hydroxyisobutyl-1-*d* isobutyl peroxide (IV)					
109.6	0.492	316	..[g]	..[g]	..[g]
(D) 1-Hydroxyisobutyl isobutyl peroxide[h] (I)					
99.4	0.476	422	96	45	3280
109.9	0.505	554	92	40	1580

[a] Temperature was controlled to better than ±0.1° and was accurate within ±0.2°. [b] Purity, exclusive of added nitrogen, was determined by standard Orsat technique. [c] Yield estimated from total volume of gas and purity, < indicates yield less than maximum value, no analysis. [d] Half-life for over-all reaction was taken as time at which one half total final volume was evolved. [e] No analysis made on decomposition gas. [f] Uncertainty due to possible leak in system. [g] Due to small sample no analysis or kinetic measurements were made. [h] Taken from Table II, ref. 1.

Results and Discussion

Two points concerning the results are immediately apparent: The rate of hydrogen evolution was considerably slower and the percentage yield of gas (total H_2, HD and D_2) was much lower than for the non-deuterated compound.[1] The determination of the value of the kinetic isotope effect is made uncertain by the fact that the compounds were not isotopically homogeneous and by the fact that the yield of gas was in the range of 23–38% of the theoretical calculated for eq. 1.

Since the 1-hydroxyisobutyl-1-*d* isobutyl-1,1-d_2 peroxide (A) was not 100% deuterated in the α-positions, the gas evolved was a mixture of D_2, HD and H_2. The theoretical composition of the gas, assuming complete reaction according to eq. 1 and no competing reactions, *i.e.*, 100% yield, can be estimated if one makes the reasonable assumption that the isobutyl-1,1-d_2 hydroperoxide (produced from alcohol which had 95% of the theoretical deuterium content for RCD_2OH) has the

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[3] J. E. Franck and E. Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934).

[4] M. J. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

[5] A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **78**, 5597 (1956).

[6] Mass spectrographic analysis by Stanford Research Institute.

[7] We wish to thank Varian Associates and Dr. James Shoolery for these analyses by nuclear magnetic resonance.

[8] The isolation of both aldehyde and alcohol from the same Bouveault–Blanc reduction mixture, the former containing deuterium in the α-position and the latter not, is of considerable mechanistic importance and will be investigated further.

[9] C. F. Wurster, L. J. Durham and H. S. Mosher, *J. Am. Chem. Soc.*, **80**, 327 (1958).

[10] It should also be noted that III and VI represent diastereoisomers. These are minor constituents and differences between such *erythro* and *threo* forms would be negligible for the present study.

composition 92% RCD_2OOH, 7% $RCHDOOH$ and 1% RCH_2OOH. The peroxyhemiacetal resulting from reaction of this mixture with isobutyraldehyde-1-*d* containing 96% deuterium in the 1-position should have the following approximate composition: 88.3% II, 3.7% V, 6.7% III, 0.3% VI, 0.9% IV and 0.04% I. In the decompositions of III and VI an isotope effect on the gas composition could reasonably be expected; assuming this to be approximately four, the expected gas composition would be approximately 90% D_2, 9% HD and 1% H_2.

The reaction of this same isobutyl-1,1-d_2 hydroperoxide with undeuterated isobutyraldehyde should give a mixture (B) of 92% V, 7% VI and 1% I. The gas from such a mixture, assuming 100% yield, should be close to 93% HD and 7% H_2. The product (C) from the isobutyraldehyde which was 96% deuterated in the 1-position and undeuterated isobutyl hydroperoxide should be 96% IV and 4% I, and should give gas which was 96% HD and 4% H_2 assuming no competing side reactions.

The isotopic distributions determined by mass spectrographic analysis[6] are reported in Table II, where it is seen that the discrepancies are large, especially in the last two examples.

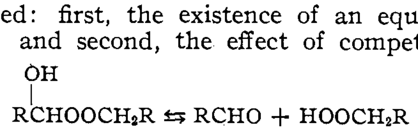
TABLE II

ISOTOPE DISTRIBUTION IN EVOLVED HYDROGEN

Temp.,[a] °C.	Total vol. gas, ml.	Isotopic distribution[e] H_2	HD	D_2	Fraction of gas
(A) 1-Hydroxyisobutyl-1-*d* isobutyl-1,1-d_2 peroxide					
99.6	12.1	< 2.5[b]	22.3	75.3	Total
109.8	18.2	2	22.7	75.4	Total
110.0	21.9	< 2[b]	21.9	76.3	Total
122.0	12.3	<10[b]	>25[c]	>65[c]	0–0.5
		< 2[b]	>25[c]	>70[c]	0.5–0.9
		< 2[b]	>22[c]	>75[c]	Last 0.1
(B) 1-Hydroxyisobutyl isobutyl-1,1-d_2 peroxide					
109.6	19.1	11	69	20	Total
(C) 1-Hydroxyisobutyl-1-*d* isobutyl peroxide					
109.6	28[d]	33.6	63.8	2.7	0–0.5
		36.4	63.5	0.1	0.5–0.75
		52.5	47.4	0.1	Last 0.25

[a] Temperature controlled to better than ±0.1° and accurate to within ±0.2° of value reported. [b] Maximum value. [c] Minimum value, small sample containing high concentration of nitrogen reduced accuracy of analysis. [d] Gas samples taken at reduced pressure, volumes estimated. [e] Relative volume per cent.

These discrepancies may be rationalized by two factors in addition to the deuterium isotope effect expected: first, the existence of an equilibrium, eq. 2; and second, the effect of competing side reactions as evidenced by the low yield of hydrogen in these decompositions.



$$\overset{\displaystyle OH}{\overset{|}{R\text{C}}}HOOCH_2R \leftrightarrows RCHO + HOOCH_2R \qquad (2)$$

Evidence has already been presented showing that an equilibrium exists between the peroxyhemiacetal I and the aldehyde and hydroperoxide from which it is made[9] (eq. 2). In the decomposition of an isotopically pure II the aldehyde formed (eq. 1) would also be identical isotopically to the aldehyde from which the peroxyhemiacetyl was originally prepared. Thus there would be no effect on the gas composition as a result of this equilibrium (eq. 2) when pure II was the starting material. But the presence of species III, IV and VI in the starting material would, together with an isotope effect favoring breaking of the C–H bond *versus* C–D bond, result in an initial gas composition which would be richer in HD and H_2 than the composition of the total gas mixture alone would indicate. This was verified in the experiment at 122° (Table II) where the initial half of the evolved gas was collected separately and analyzed. Furthermore, a careful plot of the rate of initial gas evolution showed that the first 10–20% of the gas came off faster than the remainder. The last 10% of the gas in this run was also collected separately and it did not reach the "calculated" composition. Two explanations can be advanced for this, based on competing side reactions. First, the introduction of deuterium into the molecule had reduced the decomposition rate by the route of eq. 1 by a nominal factor of 3 to 4 by virtue of the deuterium isotope effect, which thus permitted other decomposition reactions to take over. The yields of hydrogen were only 20–40% of the theoretical as compared to yields of up to 75% when non-deuterated starting material was used.[1] Thus a major portion of the starting material was destroyed by routes other than eq. 1. If the competing reactions did not discriminate between the isotopic species in the starting material, then when 90% of the reactant had been destroyed, in part by the route of eq. 1 (which shows an isotope effect), and in part by competing reactions (which did not show an isotope effect), the remaining 10% of starting material would be much nearer the original composition than that anticipated by a decomposition going entirely by eq. 1. This would be reflected in the significant amounts of H_2 and HD in the isotope composition of the gas at the end of the reaction, as was actually observed.

The predominant species reported in decomposition B, Table II, is the 1,1-dideuterated compound V. The mechanism of eq. 1, excluding the equilibrium of eq. 2, predicts no D_2 gas. Actually 20% was observed. We interpret this to mean that the equilibrium is very important. Decomposition by the mechanism of eq. 1 gives RCDO which then reacts with RCD_2OOH from the equilibrium (eq. 2) to give an important amount of II which was not in the original reaction mixture and which decomposes to give D_2. Thus D_2 results from the decomposition at the expense of HD. Since the hydrogen-containing peroxyhemiacetal V decomposes faster than II, the proportion of D_2 which forms must increase toward the end of the reaction. The observed discrepancy is therefore readily accommodated by equilibrium 2.

In decomposition C, Table II, where the predominant species is the monodeuterated material IV, the relative proportion of H_2 is increased at the expense of HD over that calculated by a process proceeding solely *via* eq. 1. This discrepancy can be accounted for by the same considerations pre-

TABLE III

VALUES FOR THE DEUTERIUM EVOLUTION REACTION FROM 1-HYDROXYISOBUTYL-1-*d* ISOBUTYL-1,1-d_2 PEROXIDES IN α-METHYLSTYRENE

Temp.,[a] °C.	$k \times 10^5$, sec.$^{-1}$ [b]	$k_D \times 10^5$, sec.$^{-1}$ [c]	k_H/k_D	A[d] $\times 10^{-7}$	ΔS^*[e]	ΔF^*[f]
(A)	1-Hydroxyisobutyl-1-*d* isobutyl-1,1-d_2 peroxide					
99.6	6.9	2.6	3.4	7.1	−24.6	30.0
109.8	18	4.8		6.5	−25.0	30.4
110.0	19	5.2	3.9[g]	5.5	−24.7	30.3
122.0	42	13.0	3.2[h]	7.6	−24.7	30.6

[a] See footnote *a*, Table I. [b] Observed rate constant for all reactions involved. [c] Rate constant for formation of deuterium. [d] Arrhenius frequency factor, sec.$^{-1}$; the Arrhenius energy of activation E_a was 21.4 kcal./mole. [e] Entropy of activation, cal./mole/degree; the enthalpy of activation, ΔH^*, was 20.8 kcal./mole. [f] Free energy of activation, kcal./mole. [g] Based upon average of two values for k_H and k_D. [h] Value for k_H obtained by extrapolation of data in ref. 1 = 4.2×10^{-4}.

sented in cases A and B. The isotope effect and the production of I *via* equilibrium 2 and RCHO formed from decomposition of IV, tend to enhance the discrepancies observed in this case more than the others.

Because of the contribution of each of these factors is not known, it is not feasible to make a quantitative evaluation of these data. In spite of these complications, however, these rate data are summarized in Table III, and should be useful in estimating a *minimum* isotope effect. The observed rate constant is corrected to give k_D by considering the yield of isotopic hydrogen, thus k_D contains a small k_H contribution.

The isotope effect is taken as the ratio of the rate constants for hydrogen[1] and deuterium evolution (k_H/k_D) assuming that compound A is 100% deuterated in the α-position. This ratio is seen to be 3.9 at 110°. If the labeled compound had been 100% deuterated in the α-position, a somewhat larger value undoubtedly would have been observed. Thus this is a minimum figure. The thermodynamic constants are also given in Table III. although their accuracy is not known because of the low yields of isotopic hydrogen. It is significant, however, that the value for the entropy of activation is clearly negative, about −25, similar to that obtained for the undeuterated compounds. The other thermodynamic values are also quite comparable to those for the undeuterated compounds.

The presence of this isotope effect and the negative entropy of activation are taken as evidence contrary to a radical cage process and in complete accord with the cyclic concerted mechanism previously postulated.[2]

Acknowledgment.—The authors wish to thank the National Science Foundation and Petroleum Research Board for financial support of this work and Dr. Harold Johnston and Dr. Russell Hardwick for valuable discussions throughout the course of this investigation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

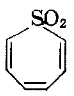
Reactions in Medium-sized Cyclic Sulfides[1]

BY C. G. OVERBERGER, PAUL BARKAN,[2] AINO LUSI[2] AND HELMUT RINGSDORF[2]

RECEIVED JANUARY 5, 1962

Dieckmann ring closure on the appropriate sulfide diesters under high dilution conditions resulted in the formation of 1-thiacycloöctane-5-one and 1-thiacyclononane-5-one. An investigation of these medium-sized ring ketosulfides disclosed sulfur–carbon ring closure in the eight- and nine-membered ring compounds. The bicyclic perchlorate salts were formed by transannular reactions.

In the course of our investigations of cyclic sulfones of type I[3] several sulfur-containing ring compounds were prepared (II, III, IV, V).[4-6] In this paper we want to report the preparation and reactions of eight- and nine-membered cyclic sulfides.



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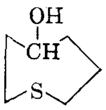

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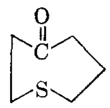

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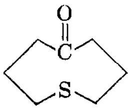
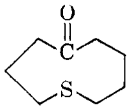


IV



V

The eight-membered ring ketosulfide IV, 1-thiacycloöctane-5-one, was prepared by the Dieckmann cyclization of diethyl γ,γ'-thiabis-*n*-butyrate (VI) under high dilution conditions, followed by hydrolysis and decarboxylation of the intermediate β-ketoester VII. The infrared spectrum of the eight-membered ring ketone IV in carbon tetrachloride showed a strong normal carbonyl absorption at 1705 cm.$^{-1}$, but in addition there was a shoulder at 1695 cm.$^{-1}$ (Table I). We have reported previously a single absorption for the seven-membered ring homolog III[3] at 1711 cm.$^{-1}$. The carbonyl doublet for the eight-membered ring was

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[1] This is the 8th in a series of papers concerned with the chemistry of cyclic sulfides and sulfones. For the previous paper in this series, see C. G. Overberger and J. M. Whelan, *J. Org. Chem.*, **26**, 4328 (1961). A preliminary account of this work was reported in an earlier communication.[4]

[2] This paper comprises parts of the dissertations submitted by Paul Barkan and Aino Lusi in partial fulfillment of the requirements for the degree of Master of Science in the Graduate School of the Polytechnic Institute of Brooklyn. Helmut Ringsdorf, present address: Institut Für Polymere, Universität Marburg, Germany.

[3] C. G. Overberger and A. Katchman, *J. Am. Chem. Soc.*, **78**, 1965 (1956).

[4] C. G. Overberger and A. Lusi, *ibid.*, **81**, 506 (1959).

[5] N. J. Leonard, T. L. Brown and T. W. Milligan, *ibid.*, **81**, 507 (1959).

[6] N. J. Leonard, T. W. Milligan and T. L. Brown, *ibid.*, **82**, 4075 (1960).