and extracted with methylene chloride (two 25-ml portions). This extract was washed with water (two 50-ml portions), dried, and concentrated under vacuum. Since gas chromatography of this crude product showed *ca.* 20% 9-decenyl 9-decenoate, it was refluxed with 40 ml of 1 *N* sodium hydroxide for 1 hr. The reaction mixture was washed with methylene chloride (two 25-ml portions), adjusted to pH 1–2 by 1 *N* hydrochloric acid, and extracted with methylene chloride (two 25-ml portions). This extract was dried, and the solvent was removed under vacuum giving 1.58 g (72%) of the crude acid.

The acid (0.618 g) in 25 ml of benzene containing 0.2 g of catalyst, tris(triphenylphosphine)rhodium(I) chloride,[24] was shaken under deuterium gas for 5 days at atmospheric pressure. The reaction mixture was extracted with 1 *N* sodium hydroxide (two 25-ml portions); the aqueous phase was adjusted to pH 1–2 with 1 *N* hydrochloric acid and extracted with methylene chloride (two 25-ml portions). This extract was dried and the solvent removed under vacuum, giving 0.55 g (89%) of the deuterated acid.

A small portion of the acid was methylated (diazomethane) and the deuterium distribution (shown in Table I) was determined from the mass spectrum of the ester, which showed that the fragments up to and including $[(CH_2)_6COOCH_3]^+$ did not contain deuterium. Thus, the deuterium present in the molecule (as deduced from the mass shift of the molecular ion) must have been incorporated on the last three carbon atoms of the aliphatic chain. The abbreviated mass spectrum[9b] of the methyl ester is: *m/e* 41 (17% relative intensity), 43 (22), 55 (21), 59 (10), 74 (100), 75 (15), 87 (52), 88 (9), 97 (4), 101 (7), 115 (2), 116 (1), 129 (4), 130 (1), 143 (9), 144 (1), 157 (4), 158 (3), 160 (3), 161 (1), 188 (1), 189 (1). (The complete intensity data for the molecular ion region are given in column 2 of Table I.) The purity of the deuterated acid was better than 99% as verified by gas chromatography (same conditions as above) of the methyl ester.

2,2-Dimethyloctanoic Acid. 2,2-Dimethyloctan-1-ol (45.8 g, from K & K Laboratories) in 150 ml of acetone was stirred with 31.9 g of chromium trioxide, 30 ml of sulfuric acid, and 120 ml of water for 2 hr. The reaction mixture was diluted with 700 ml of water and extracted with methylene chloride (two 250-ml portions). The extract was washed with water (two 250-ml portions), dried, and concentrated under vacuum. Gas chromatography showed only traces of ester; therefore, the methylene chloride solution was merely extracted with 1 *N* sodium hydroxide (two 250-ml portions). The aqueous phase was adjusted to pH 1–2 with 1 *N* hydrochloric acid, and extracted with methylene chloride (two 250-ml portions). This extract was dried, and the solvent was removed under vacuum giving 31.8 g (64%) of the acid: exact molecular weight by high-resolution mass spectrometry, 172.1444; calcd for $C_{10}H_{20}O_2$, 172.1463; nmr ($CDCl_3$) δ 11.2 (s, 1, COO*H*), 1.25 (m, 10), 1.20 (s, 6), 0.87 (t, 3, J = 5 Hz); abbreviated mass spectrum of the methyl ester (prepared with diazomethane) 41 (38), 43 (55), 55 (21), 57 (58), 69 (12), 71 (51), 85 (38), 87 (23), 102 (100), 103 (6), 111 (4), 115 (9), 127 (21), 129 (8), 157 (3), 186 (1). The base peak at *m/e* 102 (due to the McLafferty rearrangement ion) demonstrates the 2,2-dimethyl substitution. The purity of the acid (by gas chromatography, same conditions as above) was better than 99%.

Calcium 2,2-Dimethyloctanoate. 2,2-Dimethyloctanoic acid (0.5 g) was used to prepare the calcium salt by precipitation with calcium hydroxide.[22] A preliminary gas chromatographic–mass spectral experiment showed that the pyrolysate of this salt gave only one poorly shaped gas chromatographic peak. It consisted of at least three compounds, two of which were identified as 2-methyl-1-octene and 2-methyl-2-octene by a comparison of their mass spectra with those of the authentic materials. Since it was difficult to obtain adequate gc resolution for hydrocarbons of nine carbons or less using on-column pyrolysis, a large scale pyrolysis was carried out according to a published procedure.[18] Although the conditions of the large and small scale pyrolyses were quite different, it appears as though the products are the same.

2,2-Dimethyloctanoic acid (10.6 g) was refluxed with 3.24 g of calcium metal (turnings) and 1 ml of ethanolic HCl for 2.5 hr. Upon cooling, the material solidified into a yellow waxy mass. The condenser was set for distillation and the temperature was held at 500° (±50°) for 45 min. The distillate (1.12 g), analyzed by gas chromatography–mass spectrometry, consisted of 39% ethanol, 24% 1-hexene, 14% 2-methyl-1-octene, 21% 2-methyl-2-octene, and 2% ethyl 2,2-dimethyloctanoate. The mass spectra and gas chromatographic retention times (as determined by coinjection) of these compounds were identical with those of authentic material. The observed mass spectra for these five compounds are: ethanol 30 (17), 31 (100), 45 (52), 46 (15); 1-hexene 30 (4), 31 (44), 41 (100), 42 (75), 55 (81), 56 (78), 67 (8), 69 (31), 84 (30); 2-methyl-1-octene 41 (80), 43 (73), 55 (78), 56 (100), 69 (77), 70 (30), 83 (11), 84 (9), 97 (2), 98 (7), 111 (10), 126 (31); 2-methyl-2-octene 39 (28), 41 (90), 55 (65), 56 (92), 69 (100), 70 (42), 83 (13), 84 (18), 97 (2), 98 (3), 111 (5), 126 (61); ethyl 2,2-dimethyloctanoate 41(51), 43 (88), 56 (28), 57 (82), 69 (25), 71 (78), 85 (59), 88 (43), 98 (3), 101 (5), 116 (100), 117 (12), 127 (35), 129 (10), 143 (4), 155 (3), 171 (2). The ethanol and ethyl ester are artifacts resulting from the ethanolic HCl used as a catalyst.

Acknowledgments. We are grateful to Professor F. D. Greene and Dr. H.-J. Förster for helpful discussions. This work was supported by a research contract from the National Aeronautics and Space Administration (NAS-1-9684).

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[24] A. J. Birch and K. A. M. Walker, *J. Chem. Soc. C*, 1894 (1966).

Pyrolysis of Lactone Tosylhydrazone Sodium Salts

A. M. Foster and William C. Agosta*

Contribution from the Laboratories of The Rockefeller University,
New York, New York 10021. *Received December 23, 1971*

Abstract: Preparation and thermal decomposition of five lactone tosylhydrazone salts **1d–5d** are described. The products observed in each case can be accounted for by an intermediate oxycarbene (**1a–5a**) which decomposes according to Scheme I. Apart from electronic state, the intermediates involved appear to be quite similar to those generated in type I photochemical reactions of cyclic ketones.

Several investigations in the past 6 years have focused attention on photochemical transformation of ketones into products which appear to arise through intermediate oxycarbenes.[1-3] Included among these transformations have been insertion into the oxygen–hydrogen bond of solvent alcohol to form acetals,[1] addition to double bonds to give cyclopropanes,[1] dimerization,[1] reaction with oxygen to yield an ester

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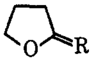
[1] P. Yates [*Pure Appl. Chem.*, **16**, 93 (1968)] gives a thorough summary of earlier work.

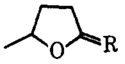
[2] W. C. Agosta and D. K. Herron, *J. Amer. Chem. Soc.*, **90**, 7025 (1968).

[3] N. J. Turro and D. M. McDaniel, *ibid.*, **92**, 5727 (1970).

carbonyl group,[1] and formation of an enol ether both by 1,2 shift of hydrogen and by hydrogen abstraction.[2] Interestingly, only cyclobutanones and bridged-ring ketones of a wide variety of structural types examined,[1,4] undergo any of these reactions on photolysis. In the investigation reported here we have sought to observe reactions of cyclic oxycarbenes prepared by an approach alternative to the photolysis of ketones. We describe below our experience with the five cyclic species **1a**–**5a**.[5] Of these, **1a**–**3a** were chosen to allow comparison with similar species available photochemically from cyclobutanones, while **4a** and **5a** are carbenes specifically not encountered[1,4] in ketone photolysis.



1



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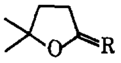
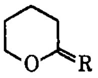
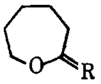


3

a, R = :
b, R = $NH_2^+X^-$
c, R = NNHTs
d, R = $N\bar{N}TsNa^+$

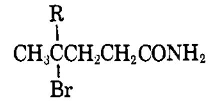


4



5

As a reliable pathway to these oxycarbenes, we selected pyrolysis of the sodium salts of tosylhydrazones. Over a number of years this method has provided a convenient source of carbene intermediates in a wide variety of chemical systems,[6-8] and there is now a useful body of information concerning reaction conditions which favor selective formation of carbenes from these precursors at the expense of alternative processes. Furthermore, synthetic routes are already available[9,10] for ester tosylhydrazones, and one[9] of these appeared particularly convenient for preparation of the precursors of **1a**–**5a**. For this approach the intermediates required are the iminolactone salts **1b**–**5b**. The unsubstituted compounds **1b**, **4b**, and **5b** were available[11] as the hydrochlorides from cyclization of the related open-chain hydroxynitriles in the presence of hydrogen chloride. The methyl-substituted **2b** was prepared, as previously reported,[12] as the hydrobromide by thermal rearrangement of γ-bromoamide **6** in benzene. We adapted this latter procedure for preparation of **3b**. In this case bromination of isocaproamide (**7**) in aqueous base gave the *N*-bromoamide **8**. Photolysis of crude **8** in benzene led to **9**, as expected,[12] and this rearranged in hot benzene to furnish **3b** as the hydrobromide. The structure of **3b** was confirmed by hydrolysis in aqueous acid to form isocaprolactone (**10**), which was identical with an authentic sample.[13]

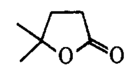


$CH_3C(R)(Br)CH_2CH_2CONH_2$

6, R = H
9, R = CH_3

$(CH_3)_2CHCH_2CH_2CONHX$

7, X = H
8, X = Br



10

Each of these salts **1b**–**5b** was now treated[9] with tosylhydrazide in alcohol to form the lactone tosylhydrazones **1c**–**5c**. Subsequent reaction with base, either sodium methoxide in methanol or sodium hydride in diethylene glycol diethyl ether, furnished the required salts, **1d**–**5d**. Both the tosylhydrazones and their salts were obtained as colorless crystalline compounds which could be stored at room temperature without incident.

These five salts **1d**–**5d** were decomposed by rapid heating to approximately 310° at 0.1 Torr in a closed system without solvent. It was known from previous experience[7] that these conditions should minimize competing processes and particularly favor clean formation of the desired oxycarbenes **1a**–**5a**. The temperature employed is somewhat higher than the customary 100–250°, since these lactone derivatives were only slowly decomposed at the lower temperatures with little gas evolution. The volatile products from each pyrolysis were analyzed and purified by vpc after separation into condensable and noncondensable fractions at −78°. Identification of the products, all of which are known compounds, rests on comparison of vpc retention times, ir, nmr, and/or mass spectra with properties of authentic samples or with detailed spectroscopic properties previously described. Convenient methods varied from case to case, and particulars for each product are given in the Experimental Section. The results are set forth in Table I, along with approximate absolute yields based on vpc measurements. From the table it is clear that pyrolysis leads to two types of compounds: rearrangement products, which include cyclic ketone, enol ether, and unsaturated aldehyde, and smaller cyclic or unsaturated hydrocarbons which have lost the elements of carbon monoxide or ketene. In the table these hydrocarbons are entered as decarbonylation products and fragmentation products, respectively.

We suggest as the simplest hypothesis accounting for these products Scheme I depicted for **3a**. Its application to **1a** and **2a** is straightforward, while for **4a** and **5a** there is included an additional step leading from the first biradical **11** to unsaturated aldyhde by hydrogen transfer. This scheme is supported by a number of earlier observations. As mentioned above, 1,2 shift of hydrogen (step a) has been seen[2] once in a photolytically generated oxycarbene. It is the most common reaction of dialkylcarbenes.[14] Homolytic cleavage of

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[4] G. Hagens, J. P. Wasacz, M. Joullié, and P. Yates, *J. Org. Chem.*, **35**, 3682 (1970).

[5] A portion of this work with **3** has been published in brief form: W. C. Agosta and A. M. Foster, *Chem. Commun.*, 433 (1971).

[6] G. L. Closs, *J. Amer. Chem. Soc.*, **84**, 809 (1962); W. Kirmse, B.-G. von Bülow, and H. Schepp, *Justus Liebigs Ann. Chem.*, **691**, 41 (1966); R. H. Shapiro, J. H. Duncan, and J. C. Clopton, *J. Amer. Chem. Soc.*, **89**, 1442 (1967); M. Rey, U. A. Huber, and A. S. Dreiding, *Tetrahedron Lett.*, 3583 (1968). A brief review is given by C. D. Gutsche and D. Redmore, *Advan. Alicycl. Chem., Suppl.* 1, 111 (1968).

[7] J. Meinwald, J. W. Wheeler, A. A. Nimetz, and J. S. Liu, *J. Org. Chem.*, **30**, 1038 (1965); R. A. Moss and J. R. Whittle, *Chem. Commun.*, 341 (1969); W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **91**, 6391 (1969); R. C. Joines, A. B. Turner, and W. M. Jones, *ibid.*, **91**, 7754 (1969); R. D. Allan and R. J. Wells, *Aust. J. Chem.*, **23**, 1625 (1970); M. Jones, Jr., S. D. Reich, and L. T. Scott, *J. Amer. Chem. Soc.*, **92**, 3118 (1970).

[8] R. J. Crawford and R. Raap, *Proc. Chem. Soc., London*, 370 (1963).

[9] R. J. Crawford and R. Raap, *Can. J. Chem.*, 43, 126 (1965).

[10] R. M. McDonald and R. A. Krueger, *J. Org. Chem.*, **31**, 488 (1966).

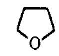
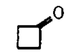
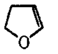
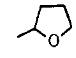
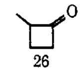
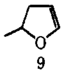
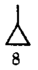
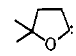
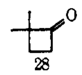
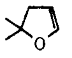
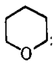
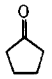
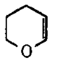
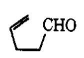
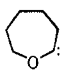
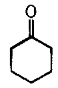
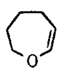
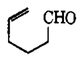
[11] H. Nohira, Y. Nishikawa, Y. Furuya, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **38**, 897 (1965).

[12] R. S. Neale, N. L. Marcus, R. G. Schepers, *J. Amer. Chem. Soc.*, **88**, 3051 (1966).

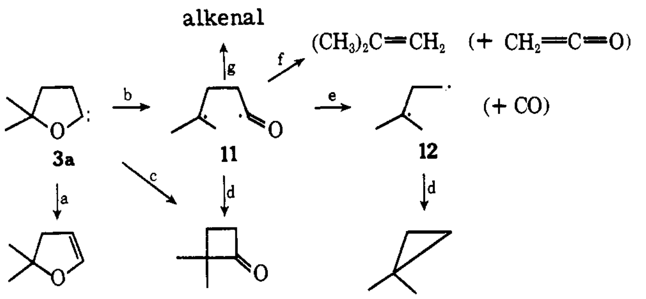
[13] This was prepared by Mr. David K. Herron following the procedure of P. K. Porter, *ibid.*, 45, 1086 (1923).

[14] L. Friedman and H. Shechter, *ibid.*, **82**, 1002 (1960); **83**, 3159 (1961).

Table I. Pyrolysis Products from **1d**–**5d**

Series	Presumed carbene	Ketone	Enol ether	Decarbonylation product	Fragmentation product	Alkenal	Total recovery, %
		Products, % yield					
1		 25	 20	 4	$CH_2{=}CH_2$ 26		75
2		 26	 9	 8	$CH_3CH{=}CH_2$ 31		74
3		 28	 11	 11	$(CH_3)_2C{=}CH_2$ 26		76
4		 61	 17			 6	84
5		 60	 11	 0.1		 16	87

Scheme I[a]



[a] The paths are: a, hydrogen migration; b, C–O cleavage; c, alkyl migration; d, collapse; e, decarbonylation; f, fragmentation; g, hydrogen transfer, applicable only to **4** and **5**.

the oxycarbene to form the alkylacyl biradical **11** (step b) has analogy in the pathway postulated for decarbonylation of both diethoxycarbene (**13**)[8] and methoxycarbene (**14**).[10] In each of these cases carbon monoxide,

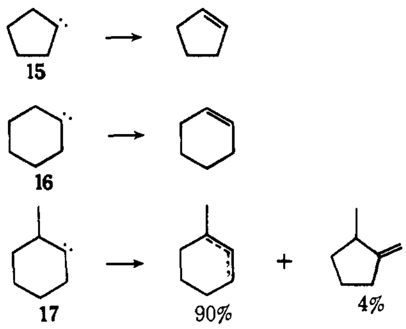
$$C_2H_5O\ddot{C}OC_2H_5 \longrightarrow C_2H_5O\cdot + CO + \cdot C_2H_5$$

13

$$H\ddot{C}OCH_3 \longrightarrow H\cdot + CO + \cdot CH_3$$

14

as well as products expected from the suggested radicals, was identified. Either collapse of biradical **11** (step d) or direct alkyl migration in the oxycarbene (step c) can account for the ketone produced. A similar choice of pathways has been discussed[8] for the reverse photochemical conversion of cyclobutanones to the related oxycarbenes, and in that case a biradical intermediate was favored. The yield of ketone is notably insensitive to substitution at C(5) in series **1**–**3**, a result implying that alkyl stabilization of an alkylacyl biradical does not influence the isomerization to ketone. In any event the particularly striking result in Table I is that ketone is a significant product in all cases. In series **4** and **5**, in fact, the yield of ketone reaches synthetically attractive levels, and the pyrolysis provides a transformation which is not otherwise convenient. In contrast, there are numerous reports that little or no alkyl migration occurs in dialkylcarbenes. Carbenes **15** and **16**, for example, yield cyclopentene and cyclohexene, respectively, as the only hydrocarbon products,[14] while the methyl homolog **17** gives 90% unrearranged cyclohexenes and only 4% ring-contracted olefin.[15]



The remaining reactions postulated from the alkylacyl biradical **11** all have familiar analogy with photochemical pathways. There is considerable evidence that the unsaturated aldehydes (step g) formed on photolysis of cyclic ketones arise through a biradical intermediate.[16] Decarbonylation (step e) with formation of cyclopropanes (step d) as well as fragmentation to olefins and ketenes (step f) both occur on irradiation of cyclobutanones, and have been accounted for there by a scheme similar to that above.[17] In the case of **4a** a biradical analogous to **12** formed on decarbonylation could close to cyclobutane or fragment to two equivalents of ethylene; neither was observed at our limit of measurement (0.1%). From **5a** this biradical could collapse to cyclopentane, which was indeed found in minute amount.

The results presented in Table I indicate that these thermal decompositions lead to a set of products commonly associated with the type I photochemical reactions of the related cyclic ketones. Accurate assess-

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(15) J. W. Wilt and W. J. Wagner, *J. Org. Chem.*, **29**, 2788 (1964).

(16) W. C. Agosta and W. L. Schreiber, *J. Amer. Chem. Soc.*, **93**, 3947 (1971), and numerous references therein. The concomitant formation of ketenes in the photochemical reaction suggests that from **4a** and **5a** propylketene and butylketene might have been formed. We attempted to trap these ketenes as methyl esters by addition of methanol to the closed reaction system within 30 sec of completion of pyrolysis of **4d** and **5d**. As little as 0.1% methyl valerate or methyl caproate would have been detected, but none was found.

(17) N. J. Turro and R. M. Southam, *Tetrahedron Lett.*, 545 (1967).

ment of the relation between the two processes, however, must await specification of the electronic states of the intermediates involved in each; at present it is attractive to assume that the intermediates are otherwise very similar. The choice of pathway (steps b + d or step c or both) for formation of the ketones remains open; we hope to clarify this point through studies now in progress.

Experimental Section

Materials and Equipment. All preparative vpc was done using a Varian Aerograph Model 700 Autoprep or Model A-90-P3 equipped with either column A, 30% Carbowax, 10 ft × $^3/_8$ in., or B, 30% QF-1, 10 ft × $^3/_8$ in., operated at column oven temperature 75–100° and helium carrier gas flow rate 120 ml/min. Analytical vpc was done using an Aerograph Model A-600-B equipped with either column C, Porapak Q, 5 ft × $^1/_8$ in., or D, 5% FFAP, 20 ft × $^1/_8$ in., operated at column oven temperature 25–145° and nitrogen carrier gas flow rate 30 ml/min. Vapor phase chromatography–mass spectrometry (gcms) was carried out using a Du Pont-CEC Model 492 mass spectrometer connected with a Varian Model 1440 gas chromatograph equipped with either column C or D, operated at helium carrier gas flow rate 30 ml/min. Ir spectra were determined on a Perkin-Elmer Model 237B spectrophotometer, and nmr spectra were determined on a Varian Model A-60 (60 MHz) or HR-220 (220 MHz) spectrometer. Melting points are corrected.

Preparation of Lactone Tosylhydrazones. A. General Procedure. A solution containing equimolar quantities of cyclic imino ether hydrochloride or hydrobromide and *p*-toluenesulfonyl hydrazine in anhydrous ethanol was stirred at 25° for 1–3 hr. The resulting mixture was diluted with benzene, filtered to remove precipitated ammonium salt, and concentrated, yielding crude lactone tosylhydrazone which was crystallized from benzene–ether. These tosylhydrazones all showed ir absorption (KBr) at approximately 3200, 1680–1640, 1590, and 1160 cm^{-1}.

B. 4-Hydroxybutyric Acid γ-Lactone Tosylhydrazone (1c). 2-Iminotetrahydrofuran hydrochloride (**1b**)[11] gave a 68% yield of **1c**: mp 177° dec; nmr (60 MHz, $CDCl_3$) δ [2.0–2.8 (m), 2.48 (s), 7 H], 4.35 (t, J = 7 Hz, 2 H), 7.38 (m, 3 H), 7.93 (d, J = 8 Hz, 2 H).

Anal. Calcd for $C_{11}H_{14}N_2O_3S$: C, 51.96; H, 5.55; N, 11.02. Found: C, 51.94; H, 5.59; N, 11.08.

C. 4-Hydroxyvaleric Acid γ-Lactone Tosylhydrazone (2c). 2-Imino-5-methyltetrahydrofuran hydrobromide (**2b**)[12] gave a 76% yield of **2c**: mp 145–147°; nmr (60 MHz, $CDCl_3$) δ 1.32 (d, J = 6 Hz, 3 H), [1.5–2.8 (m), 2.44 (s), 7 H], 4.60 (m, 1 H), 7.35 (d, J = 8 Hz, 2 H), 7.52 (m, 1 H), 7.90 (d, J = 8 Hz, 2 H).

Anal. Calcd for $C_{12}H_{16}N_2O_3S$: C, 53.72; H, 6.01; N, 10.44. Found: C, 53.90; H, 6.15; N, 10.50.

D. 4-Hydroxy-4-methylvaleric Acid γ-Lactone Tosylhydrazone (3c). 2-Imino-5,5-dimethyltetrahydrofuran hydrobromide (**3b**), prepared as detailed below, gave a 40% yield of **3c**: mp 121.5–122.5°; nmr (60 MHz, $CDCl_3$) δ 1.34 (s, 6 H), [1.5–2.9 (m), 2.43 (s), 7 H], 7.32 (m, 3 H), 7.86 (d, J = 8 Hz, 2 H).

Anal. Calcd for $C_{13}H_{18}N_2O_3S$: C, 55.30; H, 6.42; N, 9.91. Found: C, 55.18; H, 6.50; N, 10.04.

E. 5-Hydroxyvaleric Acid δ-Lactone Tosylhydrazone (4c). 2-Iminotetrahydropyran hydrochloride (**4b**) gave a 48% yield of **4c**: mp 132.5–134.5°; nmr (60 MHz, $CDCl_3$) δ 1.6–1.9 (m, 4 H), [2.2–2.6 (m), 2.45 (s), 5 H], 4.15 (t, J = 6 Hz, 2 H), 7.34 (d, J = 8 Hz, 2 H), 7.91 (m, 3 H).

Anal. Calcd for $C_{12}H_{16}N_2O_3S$: C, 53.72; H, 6.01; N, 10.44. Found: C, 53.73; H, 5.95; N, 10.47.

F. 6-Hydroxyhexanoic Acid ε-Lactone Tosylhydrazone (5c). 2-Iminooxepane hydrochloride (**5b**)[11] gave a 70% yield of **5c**: mp 128–131.5°; nmr (60 MHz, $CDCl_3$) δ 1.66 (m, 6 H), [2.3–2.6 (m), 2.43 (s), 5 H], 4.17 (m, 2 H), 7.37 (d, J = 8 Hz, 2 H), 7.74 (m, 3 H).

Anal. Calcd for $C_{13}H_{18}N_2O_3S$: C, 55.31; H, 6.43; N, 9.92. Found: C, 55.29; H, 6.34; N, 9.91.

Preparation of Sodium Salts of Lactone Tosylhydrazones. A. General Procedure. A solution was prepared from equimolar amounts of lactone tosylhydrazone and sodium methoxide in anhydrous methanol at 25° and then ether was added to precipitate the resulting sodium salt. The product was reprecipitated from methanol–ether and dried *in vacuo*, giving purified material as a fine white powder. These salts all showed ir absorption (KBr) at approximately 1675–1640, 1590, and 1225 cm^{-1}. For **3d**, satisfactory elementary analysis for carbon, hydrogen, and nitrogen is recorded below. This successful result was obtained only after a remarkable amount of effort to free the sample of traces of solvent or other impurities. Comparative pyrolyses of this analytically pure material and of samples of **3d** prepared in the usual manner revealed no detectable differences in product yield or distribution. Analytical samples were not prepared for the other salts.

B. Sodium Salt of 4-Hydroxybutyric Acid γ-Lactone Tosylhydrazone (1d). This salt was obtained from **1c** in 95% yield: mp 230° dec; nmr (60 MHz, CD_3OD) [1.8–2.7 (m), 2.37 (s), 7 H], 4.23 (t, J = 7 Hz, 2 H), 7.21 (d, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H).

C. Sodium Salt of 4-Hydroxyvaleric Acid γ-Lactone Tosylhydrazone (2d). This salt was obtained from **2c** in 79% yield: mp 269° dec; nmr (60 MHz, CD_3OD) δ 1.29 (d, J = 6 Hz, 3 H), [1.5–2.7 (m), 2.33 (s), 7 H], 4.55 (m, 1 H), 7.22 (d, J = 8 Hz, 2 H), 7.78 (d, J = 8 Hz, 2 H).

D. Sodium Salt of 4-Hydroxy-4-methylvaleric Acid γ-Lactone Tosylhydrazone (3d). This salt was obtained from **3c** in 82% yield: mp 280° dec; nmr (60 MHz, CD_3OD) δ 1.35 (s), 1.6–2.1 (m), 2.35 (s), 2.35–2.8 (m), 7.23 (d, J = 8 Hz).

Anal. Calcd for $C_{13}H_{17}N_2O_3SNa$: C, 51.30; H, 5.63; N, 9.21. Found: C, 50.97; H, 5.73; N, 9.11.

E. Sodium Salt of 5-Hydroxyvaleric Acid δ-Lactone Tosylhydrazone (4d). This salt was obtained from **4c** in 86% yield: mp 232° dec; nmr (60 MHz, CD_3OD) δ 1.5–1.9 (m, 4 H), [2.1–2.4 (m), 2.38 (s), 5 H], 4.14 (t, J = 6 Hz, 2 H), 7.27 (d, J = 8 Hz, 2 H), 7.83 (d, J = 8 Hz, 2 H).

F. Sodium Salt of 6-Hydroxyhexanoic Acid ε-Lactone Tosylhydrazone (5d). This salt was obtained from **5c** in 87% yield: mp 217° dec; nmr (60 MHz, CD_3OD) δ [1.2–2.7 (m), 2.36 (s), 11 H], 4.14 (m, 2 H), 7.18 (d, J = 8 Hz, 2 H), 7.74 (d, J = 8 Hz, 2 H).

Thermal Decomposition of Sodium Salts of Lactone Tosylhydrazones. A. General Procedure. Decomposition of the salt as a loose powder was carried out at 310° in a bulb-to-bulb distillation apparatus at an initial pressure of 0.1 Torr. Condensable products were collected at −78° and weighed, and the ratio of components was determined from their relative vpc peak areas. Yields of gaseous products were determined by comparison of vpc response to authentic samples.

B. Thermal Decomposition of the Sodium Salt of 4-Hydroxybutyric Acid γ-Lactone Tosylhydrazone (1d). The condensable portion of the pyrolysate obtained from **1d** gave two components on elution from column A. The first component, formed in 20% yield, was identified as 2,3-dihydrofuran by comparison of its ir and nmr spectra with published[18] values: nmr (220 MHz, CCl_4) δ 2.55 (t of d of d, J_{23} = 9.6 Hz, J_{34} = 2.6 Hz, J_{35} = 2.5 Hz, 2 H), 4.23 (t, J_{23} = 9.6 Hz, 2 H), 4.72 (d of t, J_{34} = J_{45} = 2.6 Hz, 1 H), 6.20 (d of t, J_{45} = 2.6 Hz, J_{35} = 2.5 Hz, 1 H). The second component, formed in 25% yield, was identified as cyclobutanone by comparison of its ir and nmr spectra with those obtained from authentic commercially available material.

The gaseous portion of the pyrolysate contained a 26% yield of ethylene and a 4% yield of cyclopropane, both identical with authentic samples by analytical vpc and gcms using column C.

C. Thermal Decomposition of the Sodium Salt of 4-Hydroxyvaleric Acid γ-Lactone Tosylhydrazone (2d). The condensable portion of the pyrolysate obtained from **2d** gave two components on elution from column A. The first component, formed in 9% yield, was identified as 2,3-dihydro-2-methylfuran by comparison of its ir and nmr spectra with published[19] values: nmr (220 MHz, CCl_4) δ 1.29 (d, J = 6 Hz, 3 H), 2.12 (m, 1 H), 2.66 (m, 1 H), 4.60 (m, 1 H), 4.73 (m, 1 H), 6.13 (m, 1 H). The second component, formed in 26% yield, was identified as 2-methylcyclobutanone by comparison of its ir and nmr spectra with published[20] values: nmr (220 MHz, CCl_4) δ 1.17 (d, J = 7 Hz, 3 H), 1.53 (m, 1 H), 2.20 (m, 1 H), 2.96 (m, 2 H), 3.27 (m, 1 H).

The gaseous portion of the pyrolysate contained a 31% yield of propene and an 8% yield of methylcyclopropane, both identical with authentic samples by analytical vpc and gcms using column C.

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D. Thermal Decomposition of the Sodium Salt of 4-Hydroxy-4-methylvaleric Acid γ-Lactone Tosylhydrazone (3d). The condensable portion of the pyrolysate obtained from **3d** gave two components on elution from column A. The first component, formed in 11% yield, was identified as 2,3-dihydro-2,2-dimethylfuran by comparison of its ir and nmr spectra with those obtained from authentic[21] material: ir (CCl_4) 1615, 1110, 1050, 685 cm^{-1}; nmr (60 MHz, CCl_4) δ 1.22 (s, 6 H), 2.28 (t, 2 H), 4.57 (q, 1 H), 6.02 (q, 1 H). The second component, formed in 28% yield, was identified as 2,2-dimethylcyclobutanone by comparison of its ir and nmr spectra with those obtained from authentic[22] material.

The gaseous portion of the pyrolysate contained a 26% yield of 2-methylpropene and an 11% yield of 1,1-dimethylcyclopropane, both identical with authentic samples by analytical vpc and gcms using column C.

E. Thermal Decomposition of the Sodium Salt of 5-Hydroxyvaleric Acid δ-Lactone Tosylhydrazone (4d). The condensable portion of the pyrolysate obtained from **4d** gave three components on elution from column B. The first component, formed in 17% yield, was identified as 3,4-dihydro-2*H*-pyran by comparison of its ir and nmr spectra with those obtained from authentic commercially available material: nmr (220 MHz, CCl_4) δ 1.84 (m, 2 H), 1.98 (m, 2 H), 3.91 (m, 2 H), 4.57 (m, 1 H), 6.28 (m, 1 H). The second component, formed in 6% yield, was identified as 4-pentenal by comparison of its ir and nmr spectra with those obtained from authentic[23] material: ir (CCl_4) 1730, 1640, 985, 910 cm^{-1}; nmr (220 MHz, CCl_4) δ 2.36 (m, 2 H), 2.48 (m, 2 H), 5.00 (m, 2 H), 5.80 (m, 1 H), 9.70 (s, 1 H). The third component, formed in 61% yield, was identified as cyclopentanone by comparison of its ir and nmr spectra with those obtained from authentic material.

The gaseous portion of the pyrolysate contained virtually no ethylene or cyclobutane, the upper limit for either of these compounds being established as 0.10% by analytical vpc using column C.

F. Thermal Decomposition of the Sodium Salt of 6-Hydroxyhexanoic Acid ϵ-Lactone Tosylhydrazone (5d). The condensable portion of the pyrolysate obtained from **5d** gave three components on elution from column B. The first component, formed in 11% yield, was identified as 2,3,4,5-tetrahydrooxepin by comparison of its ir and nmr spectra with published[24] values: nmr (220 MHz, CCl_4) δ 1.65 (m, 2 H), 1.74 (m, 2 H), 2.09 (m, 2 H), 3.83 (t, J = 5.5 Hz, 2 H), 4.60 (d of t, J_1 = 7.0 Hz, J_2 = 5.5 Hz, 1 H), 6.15 (d of t, J_1 = 7.0 Hz, J_2 = 1.5 Hz, 1 H). The second component, formed in 16% yield, was identified as 5-hexenal by comparison of its ir and nmr spectra with those obtained from authentic[25] material: ir (CCl_4) 1730, 1640, 985, 910 cm^{-1}; nmr (220 MHz, CCl_4) δ 1.71 (m, 2 H), 2.09 (m, 2 H), 2.37 (t, J = 7 Hz, 2 H), 4.98 (m, 2 H), 5.72 (m, 1 H), 9.74 (s, 1 H). The third component, formed in 60% yield, was identified as cyclohexanone by comparison of its ir and nmr spectra with those obtained from authentic material.

The gaseous portion of the pyrolysate contained a 0.13% yield of cyclopentane, which was identical with an authentic sample by analytical vpc using column C, and gcms using column D.

2-Imino-5,5-dimethyltetrahydrofuran Hydrobromide (3b). This salt was prepared from isocaproamide[26] (**7**) in 55% yield by the procedure described[12] in detail for related compounds: mp 208–210° dec from acetone; ir (KBr) 1716 (s), 1455 (m), 1098 (m), 775 (m) cm^{-1}.

Anal. Calcd for $C_6H_{12}NOBr$: C, 37.12; H, 6.24; N, 7.22. Found: C, 37.11; H, 6.37; N, 7.19.

Hydrolysis of 3b. A mixture of 150 mg of **3b**, 1.0 ml of 0.5 *M* aqueous hydrochloric acid, and 3 ml of ether was stirred at room temperature overnight and then worked up with more water and ether. The ether extracts were dried over sodium sulfate and yielded 60 mg (68%) of isocaprolactone (**10**), which was identified by comparison of its vpc retention time and ir spectrum with an authentic sample.[13]

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Kinetics of the Reaction of 1,3-Dinitrobenzene with Methoxide Ion in Methanol Solution

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Abstract: In the redox reaction of 1,3-dinitrobenzene with methoxide ion to yield *trans*-3,3′-dinitroazoxybenzene, the presence of 1,3-dinitrobenzene radical anion was detected both by electron paramagnetic resonance and electronic spectroscopy: its role as reaction intermediate was established. Kinetic parameters of this reaction were determined at 40–90° in CH_3OH solutions containing 0.14–4.90 *M* CH_3O^-. Kinetic measurements show that the rate of formation of the radical anion is equal to that of disappearance of 1,3-dinitrobenzene and to that of formation of another intermediate, which on the basis of spectroscopic evidence can be identified as a species closely related to *m*-nitronitrosobenzene. This latter species finally reacts to give the product. Hyperfine couplings for radical anion produced in dimethyl sulfoxide solution containing 0, 2, and 20 vol % CH_3OH show extensive solvation of nitro group by CH_3OH.

The reduction of nitro groups in nitroaromatics by alkoxide ions to yield the corresponding azoxy derivatives, with simultaneous oxidation of the base, is solely confined to mononitro- and *m*-dinitrobenzenes, whereas nucleophilic aromatic substitutions of nitro group are kinetically preferred by other dinitro- and

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