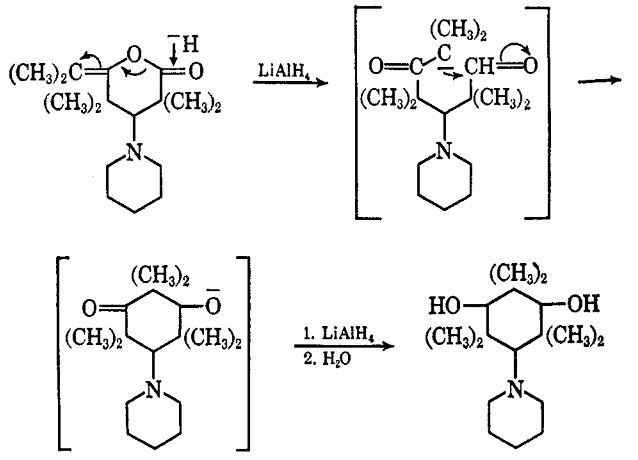
structures,[4,5] to form the corresponding aminocyclohexanediones (**2a** and **2b**) in good yields.

In our original publication the reduction of **1b** by lithium aluminum hydride to the aminocyclohexanediol (**4**) was described. It is likely that the basic reagent caused the rearrangement of the lactone to diol **4** *via* the hydroxy ketone (**5**). Hydride reduction of dione **2b** also afforded the identical glycol **4**. An analogous rearrangement during hydride reduction has been reported.[4]

Scheme II



5

4

Experimental Section

3-(Dimethylamino)-5-hydroxy-2,2,4,4,6-pentamethyl-5-heptenoic Acid δ-Lactone (1a).—This material was prepared as described previously.[3] Infrared spectrum (neat) showed 5.72 and 6.00 μ. Nmr spectrum[8] ($CDCl_3$) indicated singlets at 1.24 (3 H), 1.29 (3 H), and 1.35 (6 H) (methyl groups); singlets at 1.70 (3 H) and 1.81 (3 H) (isopropylidene group); a singlet at 2.55 (1 H) (methylidyne proton); and a singlet at 2.62 ppm (6 H) (dimethylamino group).

5-Hydroxy-2,2,4,4,6-pentamethyl-3-piperidino-5-heptenoic Acid δ-Lactone (1b).—This material was prepared as described previously.[3] Infrared spectrum (neat) showed 5.74 and 6.00 μ; nmr spectrum ($CDCl_3$) indicated singlets at 1.30 (6 H), 1.35 (3 H), and 1.39 (3 H) (methyl groups); a broad peak at 1.44 (6 H) (piperidine ring); singlets at 1.72 (3 H) and 1.83 (3 H) (isopropylidene group); a singlet at 2.51 (1 H) (methylidyne proton); and a broad peak at 2.86 ppm (4 H) (piperidine ring protons on carbon adjacent to nitrogen).

5-(Dimethylamino)-2,2,4,4,6,6-hexamethyl-1,3-cyclohexanedione (2a).—A solution of 20.4 g of **1a** and 2.0 g of sodium methoxide in 50 ml of toluene was heated for 16 hr on a steam bath. The mixture was washed with water and dried over anhydrous magnesium sulfate; the toluene was removed *in vacuo*. There remained 19.8 g of crude **2a**, mp 69–73°. One recrystallization from hexane gave 16.3 g (80%) of **2a**, mp 78–79°. Infrared spectrum (KBr) showed 5.79 and 5.91 μ. Nmr spectrum ($CDCl_3$) indicated singlets at 1.27 (9 H) and 1.30 (9 H) (methyl groups); a singlet at 2.70 (6 H) (dimethylamino group); and a singlet at 2.95 ppm (1 H) (methylidyne proton).

Anal. Calcd for $C_{14}H_{25}NO_2$: C, 70.2; H, 10.5; N, 5.9. Found: C, 70.2; H, 10.7; N, 5.7.

2,2,4,4,6,6-Hexamethyl-5-piperidino-1,3-cyclohexanedione (2b).—A solution of 34.7 g of **1b** and 2.0 g of sodium methoxide in 70 ml of toluene was heated for 16 hr on a steam bath. The mixture was washed with water and dried over anhydrous magnesium sulfate; the toluene was removed *in vacuo*. There remained 30.6 g (88%) of **2b**, mp 116.5–118°. A sample for analysis that was recrystallized from hexane melted at 118–118.5°. Infrared spectrum (KBr) showed 5.82 and 5.93 μ. Nmr spectrum ($CDCl_3$) indicated singlets at 1.25 (9 H) and 1.31 (9 H) (methyl groups); a broad peak at 1.52 (6 H) (piperidine ring); a singlet at 2.87 (1 H) (methylidyne proton); and a broad peak at 2.98 ppm (4 H) (piperidine ring protons on carbon adjacent to nitrogen).

Anal. Calcd for $C_{17}H_{29}NO_2$: C, 73.2; H, 10.4; N, 5.0. Found: C, 73.0; H, 10.5; N, 5.2.

3-(Dimethylamino)-5-hydroxy-2,2,4,4,6-pentamethylheptanoic Acid δ-Lactone (3).—A solution of 30 g of **1a** in 100 ml of cyclohexane was hydrogenated over 10 g of 5% palladium on alumina in a rocking autoclave for 5 hr at 130° and 1500 psi. The autoclave was cooled, and the contents were filtered to remove the catalyst. Examination of the filtrate by gas–liquid partition chromatography showed the presence of about 15% unchanged **1a**. Distillation through a Nestor–Faust spinning-band column gave some impure product together with 17.2 g of **3**, bp 106° (0.6 mm). This material solidified on standing, and a sample recrystallized from hexane melted at 54–56°. Infrared spectrum (KBr) showed 5.83 μ. Nmr spectrum ($CDCl_3$) indicated a pair of doublets at 0.99 and 1.04 (6 H) and multiplet at 2.01 (1 H) (isopropyl group); singlets at 1.08 (3 H), 1.12 (3 H), 1.30 (3 H), and 1.33 (3 H) (methyl groups); a singlet at 2.53 (1 H) (methylidyne proton on carbon bearing dimethylamino group); a singlet at 2.64 (6 H) (dimethylamino group); and a doublet at 3.71 ppm (1 H) (methylidyne proton).

Anal. Calcd for $C_{14}H_{27}NO_2$: C, 69.7; H, 11.3; N, 5.8. Found: C, 69.6; H, 11.5; N, 5.9.

2,2,4,4,6,6-Hexamethyl-5-piperidino-1,3-cyclohexanediol (4).—To a stirred suspension of 3.04 g (0.08 mole) of lithium aluminum hydride in 100 ml of tetrahydrofuran was added over a period of 30 min a solution of 15.0 g (0.054 mole) of **2b** in 50 ml of tetrahydrofuran. The temperature was kept at 15–25° during the addition; then the mixture was refluxed for 1 hr. The reaction mixture was cooled, and the excess hydride was destroyed by the addition of 10 ml of ethyl acetate. Then 3 ml of water, 2.5 ml of 20% sodium hydroxide solution, and 11 ml of water were added successively to the reaction mixture. The mixture was filtered, and the solid was washed with tetrahydrofuran. All filtrates were combined and evaporated to give 15.0 g of crude **4**, mp 208–214°. Recrystallization from toluene gave 12.6 g of **4**, mp 213–214°. The infrared spectrum of this material was identical with the spectrum of **4** prepared from **1b**.

Registry No.—**1a**, 10037-34-0; **1b**, 10037-35-1; **2a**, 10037-36-2; **2b**, 10037-37-3; **3**, 10037-38-4; **4**, 7538-75-2.

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[8] Nmr spectra were recorded on a Varian A-60 spectrometer at 60 Mc. Tetramethylsilane was used as an internal standard.

Selenium Chemistry. II. Stereochemistry of Vicinal Dihalide Elimination

Martin Prince and Bruce W. Bremer

Research Division, School of Engineering, and Science
New York University, University Heights,
New York, New York 10468

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The reaction of 1,2-dihalides with sodium selenide has been reported as a convenient method of preparing alkenes.[1] The synthetic utility of this reaction to the synthesis of stereoisomeric olefin derivatives has been demonstrated by the removal of bromine from 2,3-dibromobutanes by sodium selenide almost entirely in a *trans* elimination at moderate temperatures.

The nature of the elimination of bromine from 2,3-dibromobutanes by sodium selenide was investigated by treating pure *meso*-2,3-dibromobutane and *dl*-2,3-dibromobutane in both dimethylformamide and dimethyl sulfoxide. Gas chromatography was used to analyze the generated butenes.[2]

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[1] Paper I: M. Prince, B. W. Bremer, and W. Brenner, *J. Org. Chem.*, **31**, 4292 (1966).

[2] A 50-ft di-*n*-butyl maleate column was used.

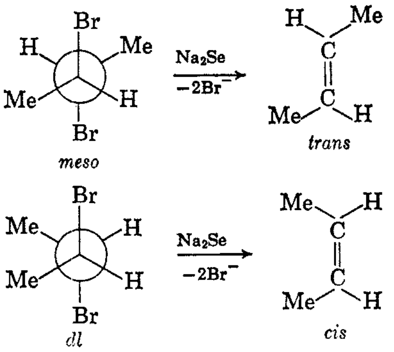
Table I summarizes the results obtained. Inspection of the table discloses that, at 75° in both dimethylformamide and dimethyl sulfoxide, *meso*-2,3-dibromobutane gives rise to a butene which is 98–99% *trans*-2-butene, and *dl*-2,3-dibromobutane gives 86–90% *cis*-2-butene. At higher temperatures, considerable rearrangement takes place. This may be due to the isomerizing effect of selenium on the butenes. It has been reported that selenium is an effective catalyst for isomerizing *cis* to *trans* olefins at high temperatures.[3] There also may be the possibility of participation of a mechanism other than the predominating one at lower temperatures. Essentially no isomerization takes place at 75° as is shown by the identical results with bromine elimination from *dl*-2,3-dibromobutane at 25°.

TABLE I
BUTENE ISOMERS RESULTING FROM BROMINE ELIMINATION

Expt	2,3-Dibromobutane	Solvent[a]	Temp, °C	% *cis*	% *trans*
1	100% *dl*	DMF	75	86.1	13.9
2	100% *dl*	DMSO	75	88.9	11.1
3	100% *meso*	DMF	75	1.0	99.0
4	100% *meso*	DMSO	75	2.0	98.0
5	100% *dl*	DMF	130	39.8	60.2
6	100% *meso*	DMF	130	20.6	79.4
7	100% *dl*	DMF	25	88.1	11.9
8	50% *dl*, 50% *meso*	DMF	75	39.1	60.9
9	50% *dl*, 50% *meso*	DMSO	75	42.4	57.6

[a] DMF, dimethylformamide; DMSO, dimethyl sulfoxide.

These results indicate that the elimination of bromine from vicinal dihalides by sodium selenide is a stereospecific *trans* elimination.



Experimental Section

Pure *dl*-2,3-dibromobutane was prepared by the addition of bromine to *cis*-2-butene (Matheson CP grade, 99.0% minimum) by the method of Young, Dillon, and Lucas.[4] The dihalide was distilled through a spinning-band column (gold plated) under 50–51-mm pressure: bp 76–77° (50–51 mm), $n^{25}D$ 1.5125. Pure *meso*-2,3-dibromobutane was prepared by the same method from *trans*-2-butene (Matheson CP grade, 99.0% minimum): bp 72–73° (50 mm), $n^{25}D$ 1.5091. The elimination reactions were carried out by addition of the 2,3-dibromobutane to a rapidly stirred slurry of sodium selenide in either dimethylformamide or dimethyl sulfoxide. Gas evolution commenced immediately and the evolved butenes were collected over water. Yields varied from 44 to 60% in these reactions.

Registry No.—*dl*-2,3-Dibromobutane, 10051-04-4; *meso*-2,3-dibromobutane, 5780-13-2.

Acknowledgment.—The authors gratefully acknowledge the support of the Selenium–Tellurium Development Association, Inc.

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[3] J. D. Fitzpatrick and M. Orchin, *J. Am. Chem. Soc.*, **79**, 4765 (1957).

[4] W. G. Young, R. Dillon, and H. Lucas, *ibid.*, **51**, 2534 (1929).

Decarboxylation Studies. III. Rate of Ketonic Decarboxylation of Lead(II) Octanoate[1a]

SHLOMO GERCHAKOV[1b] AND HARRY P. SCHULTZ

Department of Chemistry, University of Miami,
Coral Gables, Florida 33124

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The chemical literature abounds with reports on the decarboxylation of metallic carboxylates. Three references report extended efforts to study rate aspects of this reaction. Curtis, *et al.*,[2] studied the rate at which stearic acid was pyrolyzed to stearone in the presence of magnesium oxide; Leicester and Redman[3] reported that rates of ketonic decarboxylation of nickel and cobalt salts of aliphatic acids were zero order at 280°; Galwey[4] determined that decomposition of nickel benzoate obeyed zero-order kinetics.

The purpose of this Note is to report the unexpected results obtained from the study of the rate of ketonic decarboxylation of lead(II) octanoate. Kenner and Morton[5] have reported that decarboxylation of lead(II) octanoate gave 72% yield of 8-pentadecanone. Zincke[6] and Neave[7] have demonstrated that analytically pure lead(II) octanoate, unlike many metallic carboxylates, was readily prepared and recrystallized. It appeared, therefore, the lead(II) octanoate would be especially suitable for this study.

The ketonic decarboxylation of lead(II) octanoate is traditionally pictured according to the following equation.

$$(RCOO)_2Pb \longrightarrow RCOR + PbO + CO_2$$

Our studies showed that the only gaseous product was carbon dioxide, with an average mole ratio of carbon dioxide to ketone of 0.99:1.00 observed at pyrolysis temperatures of 290–310°. However, it was also observed in this investigation that the pyrolysis of lead(II) octanoate proceeded in two sharply differentiated phases. The first phase terminated after 0.5 equiv each of ketone and carbon dioxide had been obtained. The second phase did not commence until the residue (*vide infra*) from the first decarboxylation phase had been raised to a temperature of at least 360°. At this higher temperature the mole ratio of carbon dioxide to ketone was 1.51:1.00. Over-all, the total average yield of ketone was 86%, but the total average yield of carbon dioxide was 96% of theory.

The rate of decarboxylation of lead(II) octanoate was determined by collecting and measuring the volume

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[1] (a) Paper II of this series: C. Granito and H. P. Schultz, *J. Org. Chem.*, **28**, 879 (1963). (b) abstracted in part from the M.S. thesis of S. G., University of Miami, 1963.

[2] R. Curtis, A. Dobson, and H. Hatt, *J. Soc. Chem. Ind.*, **66**, 402 (1947).

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[4] A. K. Galwey, *J. Chem. Soc.*, 6188 (1965).

[5] J. Kenner and F. Morton, *Ber.*, **72**, 452 (1939).

[6] T. Zincke, *Ann.*, **152**, 11 (1869).

[7] G. B. Neave, *Analyst*, **37**, 399 (1912); *Chem. Zentr.*, [II] **83**, 1343 (1912).