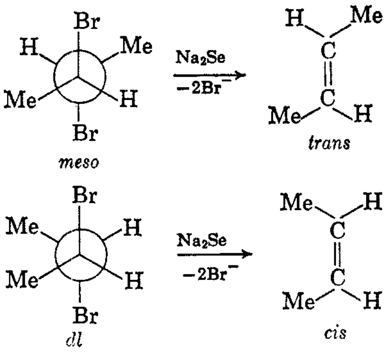
Table I summarizes the results obtained. Inspection of the table discloses that, at 75° in both dimethylformamide and dimethyl sulfoxide, *meso*-2,3-dibromobutane gives rise to a butene which is 98–99% *trans*-2-butene, and *dl*-2,3-dibromobutane gives 86–90% *cis*-2-butene. At higher temperatures, considerable 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.

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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]

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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).

[3] J. Leicester and M. J. Redman, *J. Appl. Chem.*, **12**, 357 (1962).

[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).

(corrected) of carbon dioxide evolved. The temperature bracket available for first-phase decarboxylation studies was relatively narrow (290–310°) because, below 290°, 8-pentadecanone did not completely distil from the reaction tube, and, working above 310°, the reaction rate was too rapid to study with any degree of reproducibility. In the first phase, at temperatures of 290–310°, replication of experimental results was observed; in the second phase, at temperatures of 370–380°, repeated runs gave widely divergent readings.

These results indicated that the solid residue left after completion of phase one of the reaction was possibly the anhydride of the hydroxy lead(II) octanoate, *i.e.*, a basic lead octanoate, and that the reaction might better be pictured as proceeding *via* two distinct steps.

$$2(RCOO)_2Pb \xrightarrow[300^\circ]{} (RCOOPb)_2O + RCOR + CO_2$$

$$(RCOOPb)_2O \xrightarrow[370^\circ]{} RCOR + CO_2 + 2PbO$$

This conclusion was supported by the observation that 1 equiv each of lead(II) octanoate and of lead(II) oxide, when intimately mixed and heated to *ca.* 300°, remained stable, not decarboxylating until a temperature above 365° was attained.

$$(RCOO)_2Pb + PbO \longrightarrow (RCOOPb)_2O$$

Several investigators[8-10] have suggested that ketonic decarboxylation proceeds *via* the metal salt of the corresponding β-keto acid. In this study, reactions were sacrificed during the first phase by stopping reactions after 10, 15 and 22 ml of gas (corrected volumes) had been collected, *i.e.*, during and after the first phase. The reaction residues were cooled, then placed in boiling 10% aqueous sulfuric acid solution. No evolution of any gas was observed, indicating that a β-keto acid was possibly not an intermediate in the first phase of the decarboxylation reaction, as had been earlier suggested.

Experimental Section

Equipment.—Infrared absorption spectra were recorded on a Baird Atomic Model KM I infrared spectrophotometer in chloroform concentrations of 15 mg/ml. Reactions were run in a constant temperature (±0.5°) bath filled with a 1:1 weight ratio of potassium and sodium nitrates. A 50-ml gas buret, insulated with a glass jacket, was filled with an aqueous solution of 20% sodium sulfate and 5% sulfuric acid. Such a solution has been reported[11] to have a vapor pressure of 91% that of water and also to dissolve no carbon dioxide. Vapor phase chromatograms were determined on an F & M Model 500 vapor phase chromatograph. Melting points, determined in a Thomas-Hoover apparatus, were uncorrected.

Materials.—Lead(II) octanoate was prepared and recrystallized in 81% yield according to the directions of Neave:[7] mp 83.8–84.5° (lit.[6,7] 83.5–84.5°); ν_{max} 2925, 2851 (s), 1700 (m), 1540 (s), 1464 (m), 1400 (s), 1302 (m), 1103 cm^{-1} (w). The infrared absorption spectrum and the low melting point suggest that the lead–oxygen bond may be covalent in character.

Sample Preparation.—One gram (0.002 mole) of lead(II) octanoate was weighed into a clean, dry, 34-cm Pyrex glass tube of 8-mm o.d. The upper part of the sample tube was bent into an inverted U shape, with its open end inserted into a 2 × 2 in. U tube of 11-mm o.d. which was immersed in ice and water; a sleeve of Tygon tubing served to make this joint gas tight. The open end of the U-tube was connected by means of Tygon tubing to a gas measuring buret. The top of the reaction tube itself, where it protruded from the molten salt bath, was wrapped with heating tape kept at a temperature above the boiling point (276–278°) of 8-pentadecanone to prevent condensation of the ketone before it reached the cold collection tube.

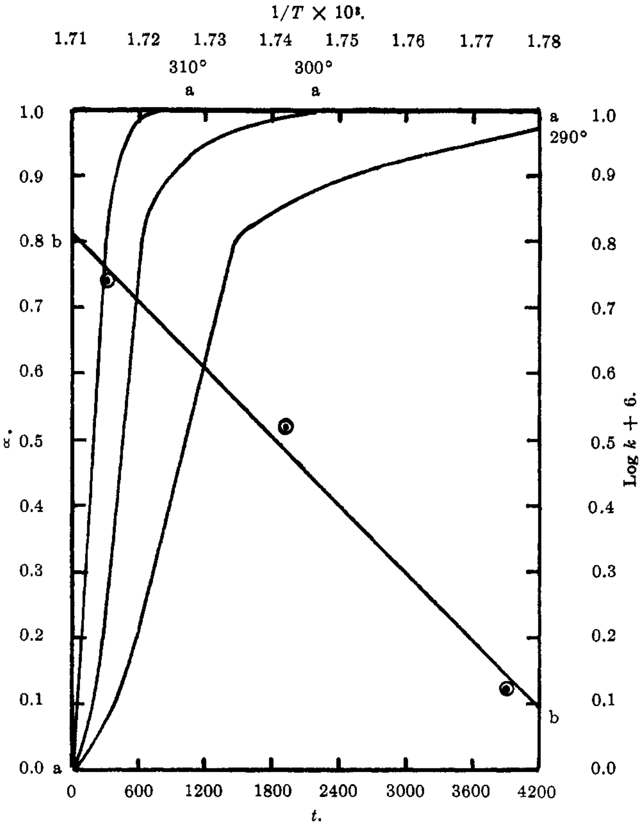

Figure 1.—(a) time (*t* in seconds) *vs.* fraction (∝) of total first-phase gas evolved; averages of four determinations at each temperature. (b) Reciprocal of absolute temperature ($1/T \times 10^3$) *vs.* log $k + 6$, for first-phase zero-order decarboxylation of lead(II) octanoate.

Results.—8-Pentadecanone obtained from the ketonic decarboxylation of lead(II) octanoate was, when removed from the collection tube, very pure: mp 42.5–43° (lit.[12] 40°), ν_{max} 1702 cm^{-1} (C=O), homogeneous by vpc analysis. These identification procedures were executed on samples obtained from reactions run at all temperatures.

Carbon dioxide gas evolved from the ketonic decarboxylation was identified by its complete absorption in Ascarite, as well as by comparison of its infrared spectrum with a known sample and with the data cited by Roberts, *et al.*[13] The measured volumes of collected carbon dioxide were corrected for both the blank caused by expansion of gas in the hot reaction tube, as well as for deviation within the gas buret from standard conditions of temperature and pressure.

Data (Figure 1a) for first-phase gas evolution were plotted as time vs. the fraction (α) of first-phase total gas evolved. The values between 0.2 and 0.8 were straight lines (decarboxylation rate not changing with time), indicating the zero-order kinetic character of the major portions of the reactions. Presuming that in the first phase of the decarboxylation 2 moles of lead(II) octanoate did indeed yield 1 mole of carbon dioxide, the specific zero-order first-phase decarboxylation rate constant[14] (k) was calculated for each temperature.

These data, averages of four determinations at each temperature, are listed in order of temperature, total mole of gas evolved, k in mole/l. sec^{-1}, time (seconds) for α of 0.5, and time for α of 0.99: 290°, 0.00107, 1.33×10^{-6}, 1050, 4800; 300°, 0.00105,

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[8] D. Neunhoeffer and P. Paschke, *Ber.*, **72**, 919 (1939).

[9] M. Stoll, *Helv. Chim. Acta*, **31**, 143 (1948).

[10] A. L. Miller, N. C. Cook, and F. C. Whitmore, *J. Am. Chem. Soc.*, **72**, 2732 (1950).

[11] L. W. Clark, *J. Phys. Chem.*, **67**, 138 (1963).

[12] G. Guckelberger, *Ann.*, **69**, 201 (1849).

[13] J. D. Roberts, D. R. Smith, and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 620 (1951).

[14] K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p 12.

3.34 × 10^{-6}, 465, 2100; 310°, 0.00103, 5.56 × 10^{-6}, 198, 600. The energy of activation for first-phase decarboxylation of lead(II) octanoate was computed by Arrhenius plot (Figure 1b) from the above data to be 47,400 cal/g mole.

Second-phase carbon dioxide evolution at 370, 375, and 380° occurred over an approximate 3-hr period at all temperatures, but data were wildly erratic and nonreproducible.

Registry No.—Lead(II) octanoate, 301-08-6; 8-pentadecanone, 818-23-5.

Anomalous Chemical Shifts in the Nuclear Magnetic Resonance Spectra of Some Neopentyl Compounds[1]

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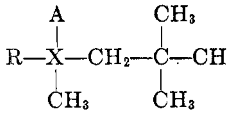
We wish to report the observation of anomalous chemical shifts in the nmr spectra determined from compounds (I–VI) containing the neopentyl group in the general arrangement depicted by the structure in Table I. These observations were made initially during preparation of compounds I–IV in connection with a study directed to another purpose.[2] Each of these four compounds gave rise to an nmr spectrum in which the signal owing to the protons of the methylene group attached to nitrogen appears at *higher* field (more shielded) than that owing to the protons of the methyl group attached to nitrogen.

TABLE I

COMPOUNDS EXAMINED



$$R{-}\overset{A}{\underset{CH_3}{X}}{-}CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3$$

Compd	X	R	A
I	N	*cis*-4-Methylcyclohexyl	Electron pair
II	N	*trans*-4-Methylcyclohexyl	Electron pair
III	N	*cis*-4-Methylcyclohexyl	Oxygen
IV	N	*trans*-4-Methylcyclohexyl	Oxygen
V	N	Methyl	Electron pair
VI	O	Electron pair	Electron pair
VII	C	Methyl	Hydrogen
VIII	C	Hydrogen	Hydrogen

In an effort to determine whether these interesting inversions of chemical shifts were merely a manifestation of some unknown effect peculiar to the rather complex system with which we were working or associated with the presence of the neopentyl groups, we carried out preparation of the known compound, N,N-dimethylneopentylamine (V)[3] and the previously unknown compound, methyl neopentyl ether (VI). In each case the nmr spectrum displayed the same chemical shift inversion of methyl and methylene signals. These data are presented in Tables I and II.

TABLE II

CHEMICAL SHIFTS[a]

Compd	CH_3X[b]	XCH_2[b]
I	136.3 (s)	128.0 (s)
II	134.8 (s)	126.8 (s)
III	180.4 (s)	177.5 (s)
IV	180.2 (s)	176.0 (s)
V	136.0 (s)	120.8 (s)
VI	196.3 (s)	177.5 (s)
VII	57.0 (d)	71.7 (d)
VIII	53.0 (t)	~72 (m)

[a] Spectra were determined from carbon tetrachloride solutions with a Varian A-60 instrument: s = singlet, d = doublet, t = triplet, m = multiplet. [b] All values are reported in cycles per second (cps) downfield from tetramethylsilane.

It is interesting that not all compounds that correspond to the general arrangement shown in Table I exhibit the chemical shift inversion. The nmr spectra determined from compounds VII and VIII, where X is carbon, have the methyl and methylene signals in normal relationship; and, it may be significant that the effect is observed only in those compounds where X is a heteroatom.

Experimental Section[4]

N-Methyl-N-*cis*- and *trans*-4-methylcyclohexylneopentylamines (I and II) and the corresponding amine oxides (III and IV) were all synthesized for use in another study. The preparative details as well as the satisfactory analytical data determined from the compounds will be reported along with the results of the work for which the compounds were originally intended.

N,N-Dimethylneopentylamine (V) was prepared according-to the procedure reported by Ingold and Patel.[3]

Preparation of **methyl neopentyl ether** (VI) was carried out by allowing sodium neopentoxide [prepared from neopentyl alcohol (35 g, 0.40 mole) and sodium metal (2.3 g, 0.20 g-atom)] to react with methyl iodide (57 g, 0.40 mole) under reflux heating during 48 hr. Careful distillation of the reaction mixture provided material from which a sample of pure VI was obtained by two successive redistillations: bp 71.5–72.0°; $n^{30}{}_D$ 1.3714; infrared spectrum, ν_{max}^{neat} no OH absorption, 2820 (OCH_3),[5] 1340, 1405 (*t*-butyl)[5] and 1115 cm^{-1} (aliphatic ether);[5] nmr, $\delta_{max}^{CDCl_3}$ 3.27 (3 *H*, singlet, CH_3O), 2.96 (2 *H*, singlet, OCH_2C), and 0.897 [9 *H*, singlet, $C(CH_3)_3$].

2,2,4-Trimethylpentane (VII) and 2,2-dimethylpentane (VIII) were purchased as analytical samples from Chemical Samples Co., Columbus, Ohio.

Registry No.—I, 10076-27-4; II, 10076-28-5; III, 10076-29-6; IV, 10076-30-9; V, 10076-31-0; VI, 1118-00-9; VII, 540-84-1; VIII, 590-35-2.

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(1) The work from which these observations arose was supported by a Petroleum Research Foundation grant, and the authors wish to acknowledge their thanks to the donors of that fund.

(2) S. I. Goldberg and F.-L. Lam, *J. Org. Chem.*, **31**, 2336 (1966).

(3) C. K. Ingold and C. S. Patel, *J. Chem. Soc.*, 67 (1933).

(4) Nmr spectra were determined at 60 Mc with a Varian Associates, Model A-60, spectrometer near 30° from carbon tetrachloride solutions containing tetramethylsilane as internal standard.

(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958; K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

Free-Radical Addition of Methanol to Perfluorocyclopentene

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Although free-radical addition of alcohols to olefins can occur by two paths,[1] the most useful reaction in-

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(1) E. V. Kirkland, *Ind. Eng. Chem.*, **52**, 397 (1960).