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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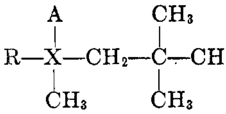
We wish to report the observation of anomalous chemical shifts in the nmr spectra determined from compounds (I–VI) containing the neopentyl group in the general arrangement depicted by the structure in Table I. These observations were made initially during preparation of compounds I–IV in connection 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



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

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°; $n^{30}\mathrm{D}$ 1.3714; infrared spectrum, $\nu_{\max}^{\text{neat}}$ 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).