

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.

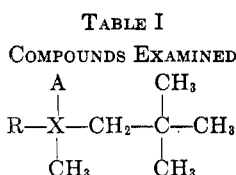
Anomalous Chemical Shifts in the Nuclear Magnetic Resonance Spectra of Some Neopentyl Compounds¹

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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



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

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.

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.

(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).

TABLE II
CHEMICAL SHIFTS^a

Compd	CH ₂ X ^b	XCH ₃ ^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 Section⁴

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_D^{20} 1.3714; infrared spectrum, ν_{max} no OH absorption, 2820 (OCH₃),⁵ 1340, 1405 (*t*-butyl)⁶ and 1115 cm⁻¹ (aliphatic ether);⁶ nmr, $\delta_{\text{max}}^{\text{CDCl}_3}$ 3.27 (3 H, singlet, CH₃O), 2.96 (2 H, singlet, OCH₂C), and 0.897 [9 H, singlet, C(CH₃)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.

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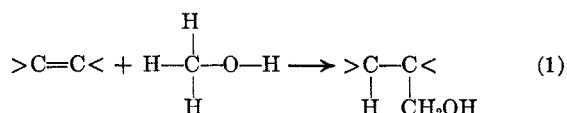
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Although free-radical addition of alcohols to olefins can occur by two paths,¹ the most useful reaction in-

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

volves the homolytic fission of an α hydrogen as illustrated in eq 1. This reaction can be initiated by ultraviolet light, or peroxides, or γ irradiation.



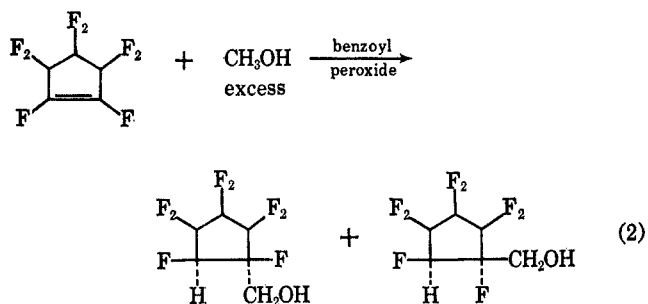
Reaction 1 has been studied thoroughly using halogenated² and nonhalogenated³ olefins with primary and secondary alcohols.

Nonhalogenated olefins give a mixture of 1:1 adduct plus telomers,³ while fluorinated olefins give a preponderance of the 1:1 adduct.² Telomerization has been reported for certain small-chain fluorinated olefins.⁴

Another contrast between the two types of olefins is their difference in behavior toward the alcohol used. While perfluoroolefins give excellent yields of the 1:1 adduct with methanol, the yield drops off sharply with ethanol and isopropyl alcohol.² The converse is true with nonhalogenated olefins.³

Apparently free-radical addition of alcohols to alicyclic fluorinated olefins does not seem to be as commonplace or clean-cut as for acyclic fluorinated olefins. When perfluorocyclohexene was used,² the free-radical addition of methanol resulted in a low conversion to a mixture of addition products plus a number of unsaturated compounds.

This result is surprising in view of our own observations in treating methanol with perfluorocyclopentene which is represented in eq 2.



The 1:1 adduct has a boiling range of 31–33° (2 mm) or 37–39° (5 mm); the analysis was satisfactory. *Anal.* Calcd for $\text{C}_5\text{H}_4\text{F}_8\text{O}$: C, 29.52; H, 1.65. Found: C, 29.67; H, 1.97. The infrared spectrum⁵ (neat) showed maxima at 2.75 and 2.98 (OH), 7.52 (CO), 8.35 (broad, CF) and 9.35 μ (OH).

The CF region in the fluorine nmr⁶ clearly showed the presence of two isomers in the ratio of 55:45. The peaks at ϕ 180.7 (singlet) and 214 (doublet) are assigned to the more abundant isomer, while the peaks at 194.9

(singlet) and 225.2 (doublet) represent the minor constituent. Both doublets have a $J_{\text{HF}} = 44$ cps which agrees for a fluorine gem to a hydrogen.⁷ No confirmation could be given for these peaks as to which represented the *cis* and *trans* isomers. Vapor phase chromatography on a 10% silicone gum rubber column packed with firebrick also confirmed the presence of two isomers in the ratio 53:47.

An attempt to add methanol to 1,2-dichlorohexafluorocyclopentene failed even though the temperature was raised to 150°. The failure of this reaction possibly results from the bulky chlorine atoms, which hinder the approach of the $\cdot\text{CH}_2\text{OH}$ radical. For example, both vinyl chloride and vinylidene chloride readily polymerize while substitution of various groups on the second carbon atom decreases the polymerizability in most cases.⁸ The steric hindrance influence of the chlorine atom has been studied by comparing the relative rates of addition of halo olefins to radicals.⁹ Although vinyl chloride or vinylidene chloride are reactive, *cis*-1,2-dichloroethylene is relatively inert.

Recent work using γ irradiation has been successful in adding ethers^{10a} and alcohols^{10b} to 1,2-dichlorotetrafluorocyclobutene and 1,2-dichlorohexafluorocyclopentene. By using high-energy particles, it is not too surprising that the stringent steric requirements are no longer paramount in order for the reaction to take place, since the energy needed for the transition state can be achieved more readily.

In a subsequent paper Muramatsu and co-workers¹¹ studied the addition of alcohols to perfluorocyclobutene by γ irradiation. With methanol the 1:1 adduct was obtained in an 84.7% yield with a preponderance of the *trans* isomer being formed. Furthermore, the yield of the isopropyl alcohol adduct shows a significant increase over that of ethanol in contrast to a previous report on acyclic halo olefins.² However, these differences could be due to the different substrates studied as well as different techniques used, although the γ -irradiation method is postulated to proceed *via* the same free-radical alcohol intermediate.

Experimental Section

Perfluorocyclopentene (42.4 g, 0.2 mole), methanol (32 g, 1.0 mole), and benzoyl peroxide (0.9 g) were added to a Pyrex tube at -60° . (The contents occupied approximately one-third of the volume of the tube.) The tube was then purged with nitrogen and sealed. For optimum results the contents were heated for 8 hr at 110° . This gave 39.1 g of a mixture of *cis*- and *trans*-1,2,2,3,3,4,4,5-octafluorocyclopentanemethanol, (80.1% yield); no telomerization was observed. When this reaction was run using a stainless steel autoclave and employing the same variables, the over-all yield dropped to 29.7%.

Registry No.—Methanol, 67-56-1; perfluorocyclopentene, 559-40-0; *cis*-1,2,2,3,3,4,4,5-octafluorocyclopentanemethanol, 10089-38-0; *trans*-1,2,2,3,3,4,4,5-octafluorocyclopentanemethanol, 10037-23-7.

(7) L. M. Jackman, in "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 86.

(8) J. K. Stille, in "Introduction to Polymer Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p 167.

(9) C. Walling, in "Free Radicals in Solutions," John Wiley and Sons, Inc., New York, N. Y., 1957, p 127.

(10) (a) H. Muramatsu and K. Inukai, *J. Org. Chem.*, **30**, 544 (1965);

(b) H. Muramatsu, K. Inukai, and T. Ueda, *ibid.*, **30**, 2546 (1965).

(11) H. Muramatsu, S. Moriguchi, and K. Inukai, *ibid.*, **31**, 1306 (1966).

(2) J. D. LaZerte and R. J. Koshar, *J. Am. Chem. Soc.*, **77**, 910 (1955).

(3) W. H. Urry, *et al.*, *ibid.*, **75**, 250 (1953).

(4) R. M. Joyce, Jr., U. S. Patent 2,559,628 (1965).

(5) Spectrum has obtained on a Perkin-Elmer Model 317 spectrophotometer.

(6) A Varian AR-60 operating at 56.4 Mc run as a 10% solution using CFCl_3 as an internal standard.