tion by alkoxide ion. The results of these calculations are given in Table VII.

TABLE VII

THERMODYNAMICS OF ACTIVATION FOR REACTIONS OF I

Product	Temp., °C.	Rate	$\Delta F^{\ddagger}_{298}$, kcal.	$\Delta S^{\ddagger}$, e.u.	$\Delta H^{\ddagger}$, kcal.
Glycol	40	1.03×10^{-5}			
	50	4.20×10^{-5}	28.0	0.8	29.3
	70	5.99×10^{-4}			
Ketone	40	7.47×10^{-5}			
	50	2.29×10^{-4}	26.8	−4.6	25.4
	70	2.52×10^{-3}			
Oxide	25	2.1×10^{6}	11		

The difference in driving force between phenyl and hydroxyl must, therefore, in this system be fairly large (>1.1 kcal). On the other hand, phenyl cannot compete with C_β–O^- when this is present to any significant extent. Indeed, the difference in driving force is so large (16 kcal.) that it is difficult to see how the action of a strong base on I or any remotely similar halohydrin could possibly result in rearrangement. Reports that such is the case[10] are, in our opinion, to be rejected on the ground that the methods of isolation caused rearrangement of epoxide subsequent to its formation.

Experimental

Action of Buffered Acetate on I.—(a) Measurement of Reaction Rate: The data appearing in Table VI were obtained by the same general procedure described above, except that simultaneously with the removal of 20-ml. aliquots for bromide ion analysis there were also removed 10-ml. aliquots for spectrophotometric analysis. These latter samples were immediately diluted with dioxane to 25 ml. in a volumetric flask and analyzed with the Beckman spectrophotometer within a period of 15 minutes.

(b) **Chromatographic Analysis of the Product.**—The product of the reaction was isolated by neutralizing a portion of the original solution with sodium bicarbonate, extracting the resulting mixture with two 30-ml. portions of chloroform and evaporating the combined extracts to dryness under reduced pressure. The weighed residue was dissolved in 40 ml. of 40% isooctane in benzene, and the solution was allowed to pass through a 12-cm. (25 g.) column of alumina (80–200 mesh, acid-washed at *p*H 3 previously ignited at 170°). Elution of the oxide–ketone fraction was accomplished by the use of 1100 ml. of benzene. The glycol was removed from the column using 100 ml. of acetone as the eluting solvent. The product composition was determined by evaporating both eluents and drying both residues to constant weight. The results of three such determinations were as follows: II–III, 94.7 ± 1.5%; IV, 5.3 ± 1.5%.

Stability of Oxide (II) in Buffered Acetate.—The oxide (II) was subjected to conditions similar to those of the preceding experiment by dissolving 653 mg. (2.4 mmoles) of oxide, 3.920 g. (28.8 mmoles) of sodium acetate trihydrate and 1.657 g. (27.6 mmoles) of glacial acetic acid in sufficient 70% dioxane to give a volume of 100 ml., and allowing the resulting solution to stand at 40° for 11 days (the time required for I to react completely under these conditions). An organic residue weighing 651.4 mg. was then isolated from the reaction mixture by the procedure described in (b) above. The material was then prepared for chromatography by first dissolving the residue in 25 ml. of 40% isooctane in benzene and pouring the solution on an 8 cm. (15 g.) column of alumina (80–200 mesh, acid-washed at *p*H 3 and ignited at 170°). By elution of the oxide–ketone fraction with 250 ml. of benzene there was obtained 641.3 mg. of material (m.p. 75–77°) identified as the oxide (II). This quantity represents a 98.5% recovery of unchanged starting material. No glycol was obtained upon further elution of the column with acetone.

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(10) M. Tiffeneau and J. Levy, *Bull. soc. chim.*, **33**, 735 (1923); **41**, 416 (1927); **49**, 1661 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Fluorination of Pentanes by Cobalt Trifluoride[1]

BY E. J. BARBER, L. L. BURGER AND G. H. CADY[2]

Perfluoro-*n*-pentane, perfluoroisopentane and perfluorocyclopentane have been prepared by the action of hot cobalt trifluoride upon vapors of the parent hydrocarbons. The crude products were separated into their components by carefu fractional distillation. Fluorination of neopentane produced numerous substances including perfluoroisopentane. No perfluoroneopentane was found among the products. Each of the crude products of fluorination contained incompletely fluorinated substances and a small proportion of unsaturated fluorocarbon. A complex mechanism which explains the known facts about the reaction of a hydrocarbon with hot cobalt trifluoride has been proposed.

As part of the program of the study of fluorine compounds in these laboratories, it became necessary to prepare a few hundred milliliters each of pure, completely fluorinated hydrocarbons. The present paper tells how the compounds were prepared and discusses the nature of the reactions involved. The properties of the fluorinated compounds are the subjects of other papers.[3]

Of the compounds studied perfluoro-*n*-pentane had been previously prepared by Fowler, *et al.*[4]; and perfluorocyclopentane had been produced by Simons and Block[5] and also by Fowler, *et al.*[4]

Experimental

The method of Fowler and co-workers[4] using hot CoF_3 as the fluorinating agent was chosen for the current work. The net reactions can be represented by the equations $CoF_2 + {}^1/_2F_2 = CoF_3$ and $24CoF_3 + C_5H_{12} = 24CoF_2 + 12HF + C_5F_{12}$.

A 36-mole quantity of cobalt trifluoride was spread into a layer about 12 mm. deep, 20 cm. wide and 2.7 meters long within a reaction vessel made by flattening copper tubing

(1) Presented at the Meeting of the American Chemical Society, Portland, Oregon, Sept. 1948.

(2) Senior author.

(3) (a) E. J. Barber, THIS JOURNAL, **73**, 4247 (1951); (b) L. L. Burger, *ibid.*, **73**, 4243 (1951); (c) G. H. Rohrback and G. H. Cady, *ibid.*, **71**, 1938 (1949).

(4) R. D. Fowler, W. Burford III, J. Hamilton, Jr., R. Sweet, C. Weber, J. Kasper and I. Litant, *Ind. Eng. Chem.*, **39**, 292 (1947).

(5) J. H. Simons and L. Block, THIS JOURNAL, **61**, 2962 (1939).

originally 10 cm. in diameter to a minimum diameter of 20 mm. Gases used in the process were caused to flow slowly in a shallow stream over the surface of this layer. The temperature of the reacting materials was controlled by regulating the current in six independent electrical heating elements surrounding the vessel. A second vessel containing sodium fluoride was used to absorb the hydrogen fluoride produced in the reaction.

The fluorinated products were condensed in two monel metal traps of 250-ml. capacity each; the first was cooled with Dry Ice and the second with liquid oxygen.

The hydrocarbon to be fluorinated was contained in a glass vaporizer of 250-ml. capacity, which could be held at a constant temperature. Gaseous nitrogen was dried over anhydrous magnesium perchlorate and then was passed through the vaporizer, thus carrying the hydrocarbon into the reaction vessel. The hydrocarbon was maintained at a temperature such that its vapor pressure was about 0.3 atm., and nitrogen was passed at a rate of about 0.2 liter per minute. Approximately 0.7 mole of pentane was fluorinated in each run. During a run, the temperature just within the entrance of the reaction vessel was held near 175° while a temperature gradient existed along the vessel, with a maximum temperature of 325° near the outlet. After a run, the CoF_2 was reconverted to CoF_3 by reaction with fluorine.

Repassing the fluorinated product over CoF_3 at about 300–325° increased the yield of completely fluorinated pentane. The repassed product was washed with water containing sodium bicarbonate and was dried over anhydrous magnesium perchlorate.

A small fractionating column was used to separate the dried fluorocarbon into three crude fractions having the boiling ranges: (1) below 20°; (2) 20–35°; and (3) above 35°. The latter two cuts were then carefully fractionated in a high efficiency helix packed column shown under conditions close to those used in the distillations to have 82 theoretical plates. The material was collected in 10-ml. fractions and those fractions shown to be identical were later combined.

Distillation curves[6] of the various crude products indicated the presence of a number of compounds, some of which were identified by their properties. Those substances boiling above 50° were not separated because they were present only in small amounts.

Neopentane gave rise to a large proportion of low boiling product. As this hydrocarbon was fluorinated, extensive chain rupture occurred with the resulting production of a mixture gaseous fluorocarbons. That portion of the product which boiled above −10° was distilled in the large fractionating column, the products being those listed in Table I.

TABLE I

FLUORINATION PRODUCTS OF THE PENTANES

Source hydrocarbon	Fluorination products	Boiling range °C.	Molecular wt. Obsd.	Molecular wt. Theor.	Product, g.
n-Pentane	cyclo-C_5F_{10}	22–23	...	250	Trace
n-Pentane	*n*-C_5F_{12}	29.3	...	288	437
n-Pentane	*n*-C_5HF_{11}#1	37.6–37.8	273	270	79
n-Pentane	*n*-C_5HF_{11}#2	40.5–40.8	276	270	159
n-Pentane	*n*-C_5HF_{11}#3	44.6–45.1	275	270	70
n-Pentane	*n*-$C_5H_2F_{10}$[m]	54.7–55.7	253	252	50
Isopentane	iso-C_5F_{12}	29.9–30.1	293	288	614
Isopentane	iso-C_5HF_{11}#1	38.2–38.7	273	270	28
Isopentane	iso-C_5HF_{11}[m]	38.7–44.1	272	270	66
Neopentane	?	−7.2 to −7.4	174	?	54
Neopentane	*n*-C_4F_{10}	−1.4 to −1.2	239	238	55
Neopentane	iso-C_4F_{10}	−0.4 to −0.2	241	238	115
Neopentane	C_4HF_9[m]	13.0–14.6	224	220	77
Neopentane	C_5F_{10}?[n]	26.8–27.3	260	250	108
Neopentane	iso-C_5F_{12}	30.0–30.1	293	288	239
Neopentane	iso-C_5HF_{11}#1				
	iso-C_5HF_{11}[m]	38.3–44.0	...	270	46
Cyclopentane	cyclo-C_5F_{10}	22.5	...	250	495
Cyclopentane	*n*-C_5F_{12}	29.2–29.3	...	288	70
Cyclopentane	cyclo-C_5HF_9	38.3–38.7	233	232	104

[m] Product is a mixture of isomers. [n] This product was not identified. It boiled at a higher temperature than cyclo-C_5F_{10} and it reacted with alkaline $KMnO_4$ solution. The high-observed molecular weight is an indication that it was contaminated with iso-C_5F_{12}.

An unusual feature of the fluorination of neopentane was that the perfluoropentane produced was identical to that obtained from isopentane (evidence: boiling point, vapor density, melting point, mixed melting point with perfluoroisopentane). During fluorination a rearrangement of the carbon skeleton occurred.

Each of the crude fluorocarbon products possessed the ability to reduce some potassium permanganate but not to react with bromine. The reactive material, presumably unsaturated fluorocarbon, was removed by refluxing the crude material for six days with an alkaline solution of potassium permanganate containing 5 g. of the salt and 2 g. of sodium hydroxide per 100 g. of water.

Unless it was removed by permanganate treatment before distillation some of the reactive material was present in the first cuts of the perfluoropentane.

The hydrocarbons subjected to fluorination were: (1) 310 g. of Phillips pure grade (99 mole %) *n*-pentane, (2) 340 g. of Phillips pure grade (99 mole %) isopentane, (3) Phillips research grade (98.93 mole %) neopentane, (4) 350 g. of Phillips technical grade (90 mole % minimum) cyclopentane.

Table I identifies the various products and indicates the amounts obtained. Those products having formulas followed by the letter (m) in the table are mixtures of isomers.

Discussion

Purity of Products.—The following lines of evidence indicate that the perfluoropentanes were nearly pure: (1) constancy of physical properties of different cuts taken during a distillation, (2) characteristically different mass spectra for the different compounds[7]; (3) absence of hydrogen atoms, as indicated by the mass spectra, (4) characteristically different infrared spectra indicating that neither the perfluoro-*n*-pentane nor the perfluoroisopentane could have contained a high proportion of the other isomer.[8]

Although conclusive evidence regarding the mechanism of reaction of cobalt trifluoride with a hydrocarbon is lacking, the experimental observations which have been made by the authors and others,[9] suggest the likelihood that certain changes take place. Among the facts which the correct mechanism must explain are: (1) presence of unsaturated materials in the products, (2) absence of polymeric products such as those formed when fluorine gas reacts with a hydrocarbon; (3) necessity for increasing the temperature as the reaction progresses; (4) ring closure to five-membered rings by *n*-heptane and by *n*-pentane; and (5) rearrangement of neopentane to isopentane during fluorination. It appears that the reaction is complex and that it may possibly involve the following types of change: (1) Formation of a free radical by a process such as $RH + CoF_3 = R\cdot + HF + CoF_2$. (2) Almost immediate destruction of the free radicals by reaction with cobalt trifluoride $R\cdot + CoF_3 = FR + CoF_2$. (3) Thermal decomposition (particularly of monofluorides) with elimination of hydrogen fluoride $C_5H_{11}F = C_5H_{10} + HF$. (4) Addition of fluorine, from CoF_3, to the double bond. (5) Removal of a double bond through ring closure. Such closure may leave a side chain.

(6) For curves order Document 3252 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(7) F. L. Mohler, E. G. Bloom, J. H. Lengel and C. E. Wise, THIS JOURNAL, **71**, 337 (1949).

(8) D. C. Smith and J. R. Nielsen, Naval Research Laboratory Report 3567, Washington, D. C., 1949, pp. 85 and 129.

(9) R. Benner, A. Benning, F. Downing, C. Irwin, K. Johnson, A. Linch, H. Parmelee and W. Wirth, *Ind. Eng. Chem.*, **39**, 329 (1947).

Perhaps carbonium ions are also produced as intermediate substances; however, their existence is not required to explain any of the observations. One can account for the formation of completely fluorinated substances by considering these steps to be repeated until all hydrogen atoms have been removed and any resulting double bonds saturated.

As fluorination progresses, the bond-strengthening influence of $-CF_2-$ groups makes the substitution of the last few hydrogen atoms more difficult; therefore, the reaction temperature must be increased.

Step five accounts for the presence of a trace of perfluorocyclopentane in the products resulting from the fluorination of *n*-pentane. Successive steps of ring closure followed by ring opening could lead to isomerization as the fluorination of the hydrocarbon proceeds. The purity of the products obtained indicates that such an isomerization is not extensive in the cases of normal and isopentane. The isomerization which occurs during the fluorination of neopentane is probably of a different type.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

Physical Properties of Perfluoropentanes[1a]

BY LELAND L. BURGER AND GEORGE H. CADY[1b]

Melting points, transition temperatures, densities and viscosities of carefully purified perfluoro-*n*-pentane, perfluoroisopentane and perfluorocyclopentane, have been determined. In many ways perfluoro-*n*-pentane is very much like its isomer perfluoroisopentane. Their properties differ somewhat, however, in directions opposite to those found for the corresponding hydrocarbons. The theoretical significance of the results is discussed.

The wide interest in the physical properties of the fluorocarbons in recent years has centered to a large extent about the low intermolecular forces which are operative in these molecules. The weakness of these forces must be due to a large extent to the shell of tightly bound fluorine atoms. Simons[2] first called attention to the high volatility of these compounds and noted the regular increase of boiling point with molecular weight. The fluorocarbon data summarized by Grosse and Cady[3] in 1947 confirmed this, and these authors showed that this regular progression with molecular weight held for many other physical properties. It was found, for example, that the viscosity of a fluorocarbon lubricant could be predicted from a knowledge of only its boiling range.

Nevertheless, it was felt that a more detailed study of the simple fluorocarbons might reveal significant differences in properties as structure and symmetry were changed. There seemed to be no good reason to conclude that this influence of structure should be parallel to that known to exist for the hydrocarbons. To investigate the effect of molecular configuration on the properties of the liquid and solid state, pure samples of the fluorocarbon pentanes were prepared.[4] Their boiling points were determined and the viscosities and densities were measured over a wide temperature range. The vapor pressures and energies of vaporization were determined by Barber in connection with other research and are the subject of another paper.[5] The pentanes were chosen because of their relative simplicity of structure, convenient liquid range and the availability of all of the pure hydrocarbons as starting materials.

(1) (a) Presented at Meeting of the American Chemical Society, Portland, Oregon, Sept., 1948; (b) Senior author.

(2) J. H. Simons and L. Block, THIS JOURNAL, **61**, 2962 (1939).

(3) A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 367 (1947).

(4) E. J. Barber, L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4241 (1951).

(5) E. J. Barber, Thesis, University of Washington, 1948.

Experimental

To avoid volatilization and to prevent condensation of water at the lower temperatures, all measurements were made in closed systems and transfers from storage vessels to the measuring apparatus were made by distillation. Stopcocks and ground joints were lubricated with "Apiezon L." Because of its extremely low volatility, this grease could not appreciably contaminate the fluorocarbons. As an added precaution, the liquids were not permitted to come in contact with the lubricated parts.

Melting points were determined from warming and cooling curves, using apparatus patterned after that of Skau[6] and described by Sturtevant.[7] A 2-g. sample of the substance to be studied was placed in a bulb equipped with a thermocouple held in a well. Surrounding the bulb was a cylindrical shell of copper, to which a second thermocouple was attached. This assembly was held in a double walled glass vessel surrounded by a bath of liquid at a known temperature. During a run the rate of temperature change of the metal shell was held at approximately 0.1° per minute by controlling the temperature of the bath and by regulating the pressure of air between the walls of the glass vessel. Temperatures of the shell and the sample were recorded alternately once a minute. From the area between the time-temperature curve of the sample and that of the outer shell an estimate of the heats involved in the various transitions and fusions was made. For this purpose the apparatus was calibrated with the hydrocarbons, *n*-pentane and isopentane, and also with mercury. The ΔH and C_p values used for the pentanes were those of Parks, Huffman and Thomas.[8,9] Data regarding mercury were taken from the International Critical Tables.

Densities were determined with two Pyrex pycnometers each consisting of a bulb to which was sealed a calibrated section of capillary tubing. Above this capillary was a small expansion bulb and finally a micro-stopcock. As a test of the apparatus the density at 25° of fractionally distilled carbon tetrachloride was measured and found to be 1.5844 g./cc., a value which compares well with 1.58426 and 1.58414 of Scatchard[10] and 1.5845 given by Timmermans and Martin.[11] Densities of the fluorocarbons were measured with

(6) E. L. Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1932).

(7) J. M. Sturtevant, Chapter X, in A. Weissberger, "Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1945.

(8) G. S. Parks, *et al.*, THIS JOURNAL, **52**, 1032 (1930).

(9) G. S. Parks and H. M. Huffman, *ibid.*, **52**, 4381 (1930).

(10) G. Scatchard, *et al.*, *ibid.*, **61**, 3206 (1939); **62**, 712 (1940).

(11) J. Timmermans and F. Martin, *J. Chim. Phys.*, **23**, 747 (1936).