reaction of perfluorobutyric acid with methyl alcohol in the presence of concentrated sulfuric acid.

In a 2-liter, 3-necked flask fitted with a mercury-sealed Hershberg stirrer, a dropping funnel and a reflux condenser, was placed 0.9 mole of ethylmagnesium iodide in 600 ml. of absolute ether and 66 g. (0.289 mole) of methyl perfluorobutyrate, dissolved in 200 ml. of absolute ether, was added dropwise with constant stirring. The mixture was allowed to stand overnight. The mixture was poured over 250 g. of ice and 0.2 mole sulfuric acid was added as a 30% solution. The ether layer was separated and the water layer was extracted with ether for five days in a continuous extractor. The ether layers were combined and dried over Drierite. The ether was removed by distillation and the mixture of products rectified. There was obtained 33.0 g. (50% yield) of 4,4,5,5,6,6,6-heptafluoro-3-hexanol, b.p. 111–113° (740 mm.), $n^{25}\text{D}$ 1.3250, and 12.0 g. (16.2%) of 3-ethyl-4,4,5,5-6,6,6-heptafluoro-3-hexanol, b.p. 140–142° (740 mm.).

Preparation of 1,1,6,6-Tetrahydro-1,6-perfluorohexanediol.—The diol was prepared by lithium aluminum hydride reduction of diethyl perfluoroadipate as described by McBee, *et al.*[5]

Preparation of 1,1,6,6-Tetrahydro-1,6-perfluorohexanediol Di-*n*-butyrate. Method A.—In a 100-ml., 3-necked flask equipped with a mercury-sealed Hershberg stirrer, dropping funnel and reflux condenser, was placed 20 g. (0.076 mole) of 1,1,6,6-tetrahydro-1,6-perfluorohexanediol and 30 ml. of dry toluene. The mixture was heated until the glycol melted (65–70°) and then 16.4 g. (0.154 mole) of perfluorobutyryl chloride was added dropwise with stirring. The rate of reaction was followed by the formation of hydrogen chloride gas. The reaction mixture was heated under reflux for three hours. After cooling, the mixture was washed with a 10% solution of potassium carbonate until the aqueous layer was free of chloride ion. The organic layer was dried over anhydrous sodium sulfate and fractionated, yielding 23.6 g. (77.3%) of diester, b.p. 112° (1.0 mm.).

Method B.—In a 200-ml., round-bottom flask fitted with a modified Dean and Stark apparatus used as a phase separator, and to which was attached a reflux condenser, was placed 30 g. (0.115 mole) of 1,1,6,6-tetrahydro-1,6-perfluorohexanediol, 22 g. (0.25 mole) of *n*-butyric acid, 40 ml. of dry toluene and 0.5 g. of sodium bisulfate. The mixture was heated under reflux for eight hours. After this time, the theoretical amount of water (4.2 ml.) had been formed. The reaction mixture was washed with a 5% solution of potassium carbonate, then with water, and finally dried over anhydrous sodium sulfate and distilled. There was obtained 35.3 g. (76.7%) of diester, b.p. 112° (1.0 mm.).

Method C.—In a 250-ml., round-bottom flask equipped with a modified Dean and Stark apparatus to which a reflux condenser was attached, was placed 55 g. (0.21 mole) of 1,1,6,6-tetrahydro-1,6-perfluorohexanediol, 12 g. (0.136 mole) of *n*-butyric acid, 26 g. (0.165 mole) of *n*-butyric anhydride, 75 ml. of dry toluene and 0.2 g. of sodium bisulfate. The mixture was heated under reflux for four hours by which time the reaction rate had slowed markedly. Up to this point 5.3 ml. of water had been collected. The reaction mixture was washed with a 5% solution of sodium carbonate, then with water, and dried over anhydrous sodium sulfate. Rectification gave 28.0 g. of a material, b.p. 95° (1.2 mm.), which was shown by carbon–hydrogen analysis and by infrared analysis to be the glycol half-ester (bands were present at 2.8 μ, characteristic of the OH stretching vibration and at 5.66 μ, characteristic of the C=O stretching vibration in this type of fluorinated ester). In addition, 33.8 g. of the diester, b.p. 111–112° (1.0 mm.), was obtained. The conversions to the half-ester and to the diester were both 40%.

Diesters of Dicarboxylic Acids with 1,1-Dihydroperfluoro Alcohols.—The general procedure, which is also applicable to the preparation of the diester from 4,4,5,5,6,6,6-heptafluoro-3-hexanol and adipyl chloride, is described below.

Bis-*n*-(1,1-dihydroperfluorobutyl)-adipate, -pimelate, -suberate, -azelate and -sebacate were prepared by treating 0.2 mole of *n*-1,1-dihydroperfluorobutanol with 0.1 mole of the appropriate acid chloride. Reaction commenced at approximately 50–80° in all cases and the reaction mixture was finally heated to 180° for two days. The rate of reaction was followed by the evolution of hydrogen chloride gas. The reaction mixture was then washed with a 5% aqueous potassium hydroxide solution until the aqueous layer gave a negative test for chloride ion. The crude diesters were dried over anhydrous magnesium sulfate and rectified. The yields of pure diesters varied from 51–77%. The properties of the pure compounds are listed in Table I.

Viscosity Measurements.—The kinematic viscosities of the diesters were determined with standard Ostwald–Cannon–Fenske type viscosimeters using the β oil standard of the American Petroleum Institute.

Flammability Tests.—The flammability screening test used was a low-pressure, spray ignition apparatus which operated on the principle of atomizing a few ml. of the test fluid using approximately 25 p.s.i. air pressure and applying an oxygen–illuminating gas torch approximately one-half inch from the nozzle into the center of the issuing spray. The length of the resulting flame determined the relative flammability of the fluid.

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[CONTRIBUTION FROM MATERIALS LABORATORY, WRIGHT AIR DEVELOPMENT CENTER, AND THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Fluorinated Esters. IV. The Effect of Neighboring Fluorine Atoms on the Ester Carbonyl Frequency[1]

BY GEORGE RAPPAPORT, MURRAY HAUPTSCHEIN, JOSEPH F. O'BRIEN AND ROBERT FILLER

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Infrared absorption spectral data of three different types of fluorine-containing esters and diesters are presented. The effect of the location of the fluorine atoms on the ester carbonyl frequency is noted and explanations for the observed effects are set forth.

Previous investigations on the infrared spectra of fluorinated esters have indicated that the ester carbonyl band exhibits a relatively large shift to higher frequencies when fluorine atoms are introduced into the molecule.[2,3] This is in contrast to the spectra of thiolesters of perfluorocarboxylic acids, discussed previously.[2]

The purpose of this study was to examine this shift for esters in detail and to determine its magnitude in relation to the proximity of the fluorine atoms to the carbonyl group. The spectra of twelve representative esters with the acid portion perfluorinated (group A), seven esters with 1,1-dihydroperfluoro alcohol portions (group B), and six almost completely fluorinated esters (group C), were taken. The wave lengths of the bands due to

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[1] Opinions expressed are those of the authors and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

[2] M. Hauptschein, C. S. Stokes and E. A. Nodiff, THIS JOURNAL, 74, 4005 (1952).

[3] M. Hauptschein, J. F. O'Brien, C. S. Stokes and R. Filler, *ibid.*, 75, 87 (1953).

C=O stretching vibrations for these compounds are shown in Table I. The accuracy is considered to be ±0.02 micron.

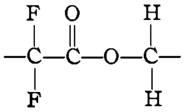
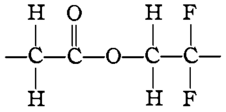
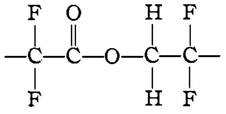
TABLE I

INFRARED SPECTRA OF FLUORINATED ESTERS AND DIESTERS

Compound	Carbonyl stretching vibration wave length, μ
Group A[a]	
$C_3F_7CO_2CH_2CH_3$	5.60
$CF_3CO_2(CH_2)_5O_2CCF_3$	5.58
$C_3F_7CO_2(CH_2)_3O_2CC_3F_7$	5.60
$C_3F_7CO_2(CH_2)_4O_2CC_3F_7$	5.58
$C_3F_7CO_2(CH_2)_5O_2CC_3F_7$	5.60
$C_3F_7CO_2(CH_2)_6O_2CC_3F_7$	5.59
$C_3F_7CO_2(CH_2)_{10}O_2CC_3F_7$	5.60
$C_5F_{11}CO_2(CH_2)_5O_2CC_5F_{11}$	5.59
$C_7F_{15}CO_2(CH_2)_5O_2CC_7F_{15}$	5.60
$C_9F_{19}CO_2(CH_2)_5O_2CC_9F_{19}$	5.60
$C_2H_5CH(CH_3)O_2C(CF_2)_4CO_2CH(CH_3)C_2H_5$	5.60
n-$C_4H_9O_2C(CF_2)_4CO_2C_4H_9$	5.57
Group B[a]	
$C_3H_7CO_2CH_2CF_3$	5.66
$C_3F_7CH_2O_2C(CH_2)_4CO_2CH_2C_3F_7$	5.66
$C_3F_7CH_2O_2C(CH_2)_5CO_2CH_2C_3F_7$	5.65
$C_3F_7CH_2O_2C(CH_2)_6CO_2CH_2C_3F_7$	5.66
$C_3F_7CH_2O_2C(CH_2)_7CO_2CH_2C_3F_7$	5.66
$C_3F_7CH_2O_2C(CH_2)_8CO_2CH_2C_3F_7$	5.66
$C_3H_7CO_2CH_2(CF_2)_4CH_2O_2CC_3H_7$	5.67
Group C[a]	
$C_3F_7CO_2CH_2CF_3$	5.55
$C_3F_7CO_2CH_2C_3F_7$	5.54
$C_7F_{15}CO_2CH_2C_3F_7$	5.52
$C_3F_7CH_2O_2C(CF_2)_3CO_2CH_2C_3F_7$	5.53
$C_3F_7CO_2CH_2(CF_2)_3CH_2O_2CC_3F_7$	5.53
$C_3F_7CO_2CH_2(CF_2)_4CH_2O_2CC_3F_7$	5.53

[a] The preparation, characterization and properties of almost all of these compounds have been given in previous papers in this series: group A—see R. Filler, J. F. O'Brien, J. V. Fenner and M. Hauptschein, THIS JOURNAL, **75**, 966 (1953); group B—ref. 5; group C—ref. 3.

Rasmussen and Brattain have pointed out that in the case of non-fluorinated unconjugated esters, electronegative α-substituents, by virtue of the inductive effect, may shift the ester C=O band down as far as 5.70 microns.[4] Since fluorine is the most *electronegative* element, the comparatively much larger shifts of the carbonyl frequency noted here is not too surprising. All esters and diesters with a perfluorinated cluster alpha to the carbonyl group (*i.e.*, in the acid portion) exhibit a C=O band at 5.59 ± 0.02 microns. When fluorine was located in the alcohol portion only, this band was observed at 5.66 ± 0.02 microns. This is a significant shift from the normal ester value of 5.75 μ,[4] especially since the α-substituents on the alcohol part of the molecule were hydrogen atoms. In the case of the almost completely fluorinated esters this absorption band was located at 5.53 ± 0.02 microns. Thus, wave length assignments within very narrow limits are possible as follows

Grouping	Wave length of C=O band, μ
	5.59 ± 0.02
	5.66 ± 0.02
	5.53 ± 0.02

In order to establish in an unambiguous fashion the magnitude of the shift of the carbonyl band, the spectrum of ethyl butyrate was compared with that of its three fluorine-containing analogs.[3,5] The spectra of these four esters are shown in Fig. 1. Ethyl butyrate itself exhibits a C=O band at 5.75 microns. It may be noted (see Table I) that a shift of 0.15 micron to shorter wave lengths resulted from the replacement of the hydrogens by fluorine in the acid portion of the molecule (*i.e.*, ethyl perfluorobutyrate). A corresponding shift of 0.09 micron was observed for trifluoroethyl butyrate, where the fluorine is located in the alcohol portion. For trifluoroethyl perfluorobutyrate this shift was 0.20 micron.

The cause of the large shifts in the case of esters of perfluorocarboxylic acids has been explained in some detail in terms of the strong inductive effect of the very electronegative perfluoroalkyl groups.[2] The significant shift of 0.09 micron due to the fluorine atoms in the alcohol portion, *i.e.*, the 1,1-dihydroperfluoroalkyl group, is most interesting. There is no question that the inductive displacement due to the perfluoroalkyl moiety has been weakened by the alpha methylene group. However, the effect is still transmitted to a considerable extent by virtue of the polarizability of the intervening C–O linkage. The shift due to fluorine in both the acid and alcohol portions of the molecule is not quite additive. This may be explained on the basis that the polarizability of the C–O bond is decreased to a certain extent when the hydrogen atoms are replaced by fluorines in the acid portion, thereby diminishing the ability of the alkoxy (*i.e.*, C–O) bond to transmit the inductive effect.

The infrared spectra were obtained on a Baird Associates infrared double beam recording spectrophotometer equipped with a rock-salt prism. Sandwich type cells were used to press out the liquid samples between the rock-salt plates sufficiently thin to yield a sharp ester carbonyl band. The upper spectral curves of Fig. 1 were taken in this manner, while the lower curves were taken in a cell of 0.0043 cm. thickness. The spectrophotometer was carefully calibrated at all times, and the wave lengths read directly from the record were corrected for any possible temperature or mechanical effects by noting the deviation from various known bands of pure samples. The reproducibility for the carbonyl bands was within ±0.02 μ. A Perkin–Elmer spectrometer calibrated by the method of

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(4) R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

(5) R. Filler, J. V. Fenner, C. S. Stokes, J. F. O'Brien and M. Hauptschein, *ibid.*, **75**, 2693 (1953).

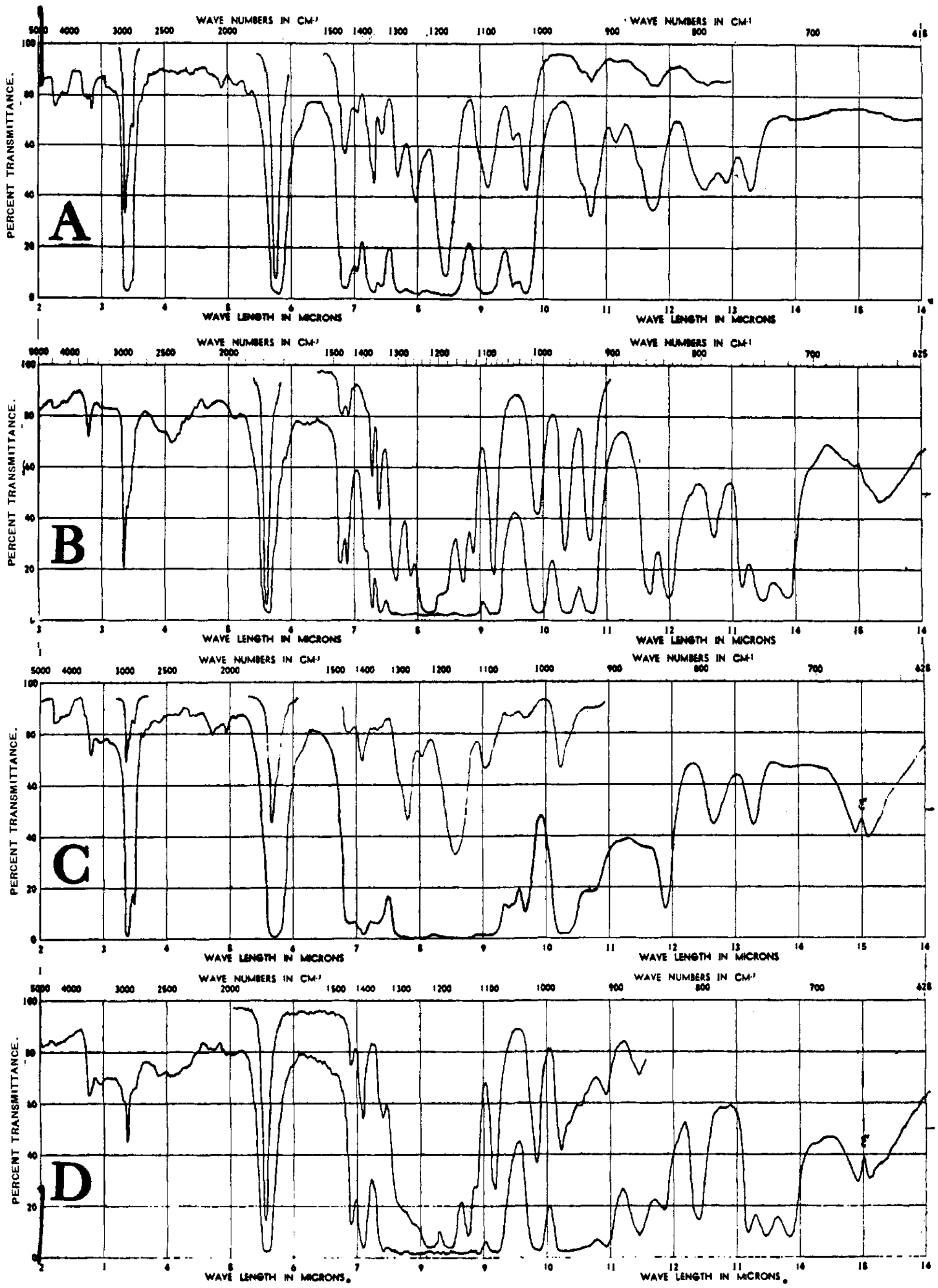

Fig. 1.—Infrared absorption spectra of: $C_3H_7CO_2C_2H_5$ (A); $C_3F_7CO_2CH_2CH_3$ (B); $C_3H_7CO_2CH_2CF_3$ (C); $C_3F_7CO_2CH_2CF_3$ (D).

McKinney and Friedel,[6] was used as a calibration check and the agreement with the Baird instrument was within ±0.02 μ in all cases tried.

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[6] D. S. McKinney and R. A. Friedel, *J. Optical Soc. Am.*, **38**, 222 (1948).