n the preparation of II. Six grams (0.053 mole) of ketene divinylacetal and 6.35 g. (0.053 mole) of 2-nitro-1-butanol were used. Upon fractional distillation, 5.2 g. (42.5%) of the orthoester III was collected, b.p. 90–93° at 2 mm., $n^{25}D$ 1.4480.

Anal. Calcd. for $C_{10}H_{17}NO_5$: C, 51.95; H, 7.41; N, 6.06. Found: C, 51.92; H, 7.70; N, 6.37.

Divinyl 3-Nitro-2-butyl Orthoacetate (IV).—The procedure for the preparation of II was followed. Five grams (0.044 mole) of ketene divinylacetal and 5.35 g. (0.044 mole) of 3-nitro-2-butanol reacted to yield 6.58 g. (63%) of divinyl 2-nitro-1-butyl orthoacetate, b.p. 85–86° at 2 mm., $n^{26}D$ 1.4512.

Anal. Calcd. for $C_{10}H_{17}NO_5$: C, 51.95; H, 7.41; N, 6.06. Found: C, 51.70; H, 7.55; N, 6.35.

Hydrolysis of the Orthoesters II, III and IV.—Each of these orthoesters was hydrolyzed by treatment of 1–2-g. samples of the orthoester with 3 drops of a 1% aqueous solution of sulfuric acid. The evolved acetaldehyde was collected and identified as its 2,4-dinitrophenylhydrazone and the corresponding nitroalkyl esters identified by physical properties previously reported in the literature.

Polymerization Studies.—Approximately 1-g. samples of divinyl β-nitroethyl orthoacetate (II), divinyl 2-nitro-1-butyl orthoacetate (III) and divinyl 3-nitro-2-butyl orthoacetate (IV) were placed in screw cap vials and a small amount of benzoyl peroxide was added to each. The vials were then immersed in an oil-bath maintained at 70°.

After 2 days, compound II had turned dark brown and viscous. The sirupy liquid was dissolved in 5 ml. of acetone and poured with stirring into 20 ml. of cold water. A finely divided brown precipitate was collected and dried. It was purified twice by dissolving it in acetone and precipitating into water. The polymer had no definite softening point but began to darken at about 100°.

At the end of 8 days, compound III had become dark and viscous. The solid was collected and purified in the same manner as described above. The dark brown polymer softened and darkened when heated above 115°.

Compound IV did not polymerize even after a heating period of ten days.

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Spectral Properties of Fluorine-containing Conjugated Esters[1]

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In a previous paper,[3] infrared absorption spectral data were presented for three types of fluorine-containing esters. The effect of the location of the fluorine atoms on the ester carbonyl frequency was noted and wave lengths were assigned for the C=O stretching vibrations. In particular, the spectrum of ethyl butyrate was compared with those of ethyl perfluorobutyrate, trifluoroethyl butyrate and trifluoroethyl perfluorobutyrate.

It was of interest, therefore, to introduce a vinyl group into the acid portion of each of these esters and to observe the effect of the resultant conjugation on the ester carbonyl frequency. In Table I the carbonyl stretching vibration for each of the conjugated esters is compared with that of the corresponding ethyl butyrate of which it is a vinylog.[4] The accuracy is considered to be ±0.02 μ.

TABLE I

Compound	C=O stretching vibration wave length, μ	Compound	C=O stretching vibration wave length, μ
$C_3H_7CO_2C_2H_5$	5.75	$C_3H_7CH{=}CH{-}CO_2C_2H_5$	5.81
$C_3H_7CO_2CH_2CF_3$	5.66	$C_3H_7CH{=}CH{-}CO_2CH_2CF_3$	5.74
$C_3F_7CO_2C_2H_5$	5.60	$C_3F_7CH{=}CH{-}CO_2C_2H_5$	5.75
$C_3F_7CO_2CH_2CF_3$	5.55	$C_3F_7CH{=}CH{-}CO_2CH_2CF_3$	5.67

Rasmussen and Brattain[5] have noted that conjugation of the ester C=O with C=C shifted the carbonyl band to longer wave lengths.

Ethyl butyrate and its vinylog, ethyl 2-hexenoate, illustrate this shift of the C=O band (5.75 μ to 5.81 μ). A similar shift of 0.08 μ is observed for the trifluoroethyl butyrate–trifluoroethyl 2-hexenoate pair. In this case, the inductive effect of the trifluoromethyl group is independent of the opposing conjugative effect. Thus, the fluorine atoms exert about the same influence on the C=O frequency that they would were conjugation not present. In earlier papers[3,6] the role of the inductive effect of the perfluoroalkyl group in shifting the C=O band to shorter wave lengths was discussed.

In ethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, $C_3F_7CH{=}CH{-}CO_2C_2H_5$, however, the inductive effect of the heptafluoropropyl group, transmitted through the vinyl linkage, is strongly opposed by resonance-stabilized conjugation.

There is sufficient evidence to substantiate this weakening of the inductive effect. Walborsky and Schwarz[7] determined the dissociation constant of 4,4,4-trifluorocrotonic acid as 7.1×10^{-4} in contrast with 5.8×10^{-1} for trifluoroacetic acid.[8] Analogous results have been reported for $C_3F_7CH{=}CH{-}CO_2H$[9] and $C_3F_7CO_2H$.[8] It has also been demonstrated[7] for ethyl trifluorocrotonate, that resonance of the carbethoxy group with the double bond, rather than the inductive effect, plays the dominant role in directing the addition of various reagents.

The observed C=O stretching frequency of $C_3F_7CH{=}CH{-}CO_2C_2H_5$ substantiates these results. While a shift of 0.15 μ to shorter wave lengths resulted from replacement of the hydrogens by fluorine in the acid portion of ethyl butyrate, a markedly smaller shift of only 0.06 μ is observed in the corresponding conjugated esters. A similar effect was noted by Rasmussen and Brattain in esters of nitrobenzoic acids.[5]

(1) Opinions expressed are those of the author and do not necessarily express the official opinions of the U. S. Air Force or the Wright Air Development Center.

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(4) The infrared spectra referred to in this article have been deposited as Document number 4147 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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Finally, trifluoroethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, $C_3F_7CH{=}CH{-}CO_2CH_2CF_3$, exhibits the C=O band at 5.67 μ. This is readily accounted for by considering the influence of the CF_3 group of the alcohol portion, which is independent of the conjugated system, as mentioned earlier.

The ultraviolet absorption spectra of ethyl 2-hexenoate. trifluoroethyl 2-hexenoate, and the ethyl heptafluoro-2-hexenoate were also determined and similar maxima were observed in the region of 208–210 mμ, in agreement with previous findings[10] for unfluorinated esters of this type.

Ethyl 2-hexenoate was obtained from 2-hexenoic acid, which was prepared by a known method.[11] Trifluoroethyl 2-hexenoate, a new compound, was obtained from 2-hexenoyl chloride and trifluoroethanol. The ethyl heptafluoro-2-hexenoate was prepared by a recently reported procedure.[9] Trifluoroethyl heptafluoro-2-hexenoate, also a new compound, was obtained from the acid chloride and trifluoroethanol.

Experimental

Ethyl 2-Hexenoate.—2-Hexenoic acid and its ethyl ester were prepared by previously described procedures.[11,12]

Trifluoroethyl 2-Hexenoate.—2-Hexenoyl chloride was prepared from the acid and thionyl chloride. The acid chloride, b.p. 118–122°, was used directly in the next step without further purification.

In a 100-ml., r.b. flask fitted with a dropping funnel and a reflux condenser was placed 15 g. (0.15 mole) of trifluoroethanol. The alcohol was heated to boiling and then 22.0 g. (0.165 mole) of 2-hexenoyl chloride, was added dropwise over a period of 15 minutes. The mixture was heated under reflux for five hours. The reaction could be followed by the rate of evolution of hydrogen chloride. The mixture was washed with a 10% solution of sodium bicarbonate until the aqueous layer was free of chloride ion, then with water, and finally the organic layer was dried over anhydrous sodium sulfate. Distillation gave 21 g. (71.4% yield) of ester, b.p. 65–66° (20 mm.), $n^{25}D$ 1.3870, d^{25}_4 1.111. Calcd. for $C_8H_{11}F_3O_2$: C, 48.98; H, 5.65. Found: C, 48.97; H, 5.52.

Ethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate.—This ester was prepared by dehydration of ethyl 3-hydroxy-4,4,5,5,6,6,6-heptafluorohexanoate,[9] which was obtained by the Reformatsky reaction using perfluorobutyraldehyde and ethyl bromoacetate.[9] Perfluorobutyraldehyde was prepared in 68% yield by reduction of ethyl heptafluorobutyrate with lithium aluminum hydride at −70° using the inverse addition technique, as described by Pierce and Kane.[13]

Trifluoroethyl 4,4,5,5,6,6,6-Heptafluoro-2-hexenoate.—4,4,5,5,6,6,6-Heptafluoro-2-hexenoic acid was obtained by saponification of the ethyl ester.[9]

The heptafluoro-2-hexenoic acid (18 g., 0.075 mole) was converted to the acid chloride by refluxing with excess benzoyl chloride (25 g., 0.178 mole); yield 14.3 g. (73.7% yield), b.p. 65–73°. It was used directly for the next step.

To 5.0 g. (0.05 mole) of boiling trifluoroethanol in a r.b. flask fitted with a reflux condenser and a dropping funnel, was added dropwise 14 g. (0.054 mole) of the acid chloride. The mixture was heated under reflux for 12 hours by which time the evolution of hydrogen chloride had ceased. The mixture was taken up in ether, washed first with a 10% solution of sodium bicarbonate until the aqueous layer was free of chloride ion, then with water, and finally dried over anhydrous magnesium sulfate. Distillation afforded 6 g. (37.3% yield) of trifluoroethyl 4,4,5,5,6,6,6-heptafluoro-2-hexenoate, b.p. 132°, $n^{25}D$ 1.3258. Calcd. for $C_8H_4F_{10}O_2$: C, 29.83; H, 1.25. Found: C, 30.50; H, 1.36.

Infrared Absorption Spectra.—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 were taken in this way, while the lower curves were taken in a cell of 0.028 cm. thickness. The spectrophotometer was carefully calibrated 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.

Ultraviolet Absorption Spectra.—The spectra of three esters, ethyl 2-hexenoate, trifluoroethyl 2-hexenoate, and the ethyl heptafluoro-2-hexenoate, at concentrations of 20–30 γ/ml. in absolute methanol, were obtained with a Cary recording spectrophotometer. In all three cases, maxima were observed in the region of 208–210 mμ.

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Degradation of the Optical Isomers of Isoleucine and Alloisoleucine to *d*- and *l*-α-Methylbutyraldehyde

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The proposed mechanisms[1] for the Strecker degradation of α-amino acids by carbonyl compounds require that an amino acid with an asymmetric carbon in the β-position retain its optical activity during the reaction. However, this requirement does not appear to have been tested experimentally and since we had available the optical isomers of isoleucine and alloisoleucine[2] such a test seemed desirable.

Treatment of the optical isomers of isoleucine and alloisoleucine with ninhydrin resulted in each case in the production of optically active α-methylbutyraldehyde, isolated as the 2,4-dinitrophenylhydrazone. L-Isoleucine and D-alloisoleucine gave rise to the *d*-derivative; L-alloisoleucine and D-isoleucine yielded the *l*-enantiomorph. From the rotation data compiled in Table I it can be seen that the optical purity of the isolated com-

TABLE I

PROPERTIES OF 2,4-DINITROPHENYLHYDRAZONES OF α-METHYLBUTYRALDEHYDE OBTAINED BY DEGRADATION OF ISOLEUCINE AND ALLOISOLEUCINE

Compound degraded	Properties of 2,4-dinitrophenylhydrazones M.p., °C.	$[\alpha_D]$, *c* 1 in acetic acid	$[\alpha_D]$, *c* 5 in acetone	$[\alpha]_D$, *c* 0.73 in chloroform
L-Isoleucine	135–137	+29.5°		
D-Isoleucine	135–137	−29.7		
L-Alloisoleucine	135–137	−30.0	−35.0°	−35.7°
D-Alloisoleucine	135–137	+29.9	+35.0[a]	+35.5[b]

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