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.

Acknowledgment.—The author wishes to thank Mrs. Nora Srp for conducting the elemental analyses and for obtaining the infrared spectra.

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[10] J. Cason, N. L. Allinger and G. Sumrell, *J. Org. Chem.*, **18**, 850 (1953); J. Cason and G. Sumrell, *ibid.*, **16**, 1181 (1951).

[11] A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.*, 2351 (1928).

[12] B. R. Baker, M. V. Querry, S. R. Safir and S. Bernstein, *J. Org. Chem.*, **12**, 144 (1947).

[13] O. R. Pierce and T. G. Kane, THIS JOURNAL, **76**, 300 (1954).

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

BY WILLIAM S. FONES

RECEIVED NOVEMBER 21, 1953

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

	Properties of 2,4-dinitrophenylhydrazones			
Compound degraded	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]

[a] E. J. Badin and E. Pacsu, THIS JOURNAL, **67**, 1352 (1945), report $[\alpha]_D$ +32.1° (c 4.99 in acetone) and m.p. 132.5–133°. [b] P. A. Plattner and U. Nager, *Helv. Chim. Acta*, **31**, 2200 (1948), report $[\alpha]_D$ +19.9 (c 0.730 in chloroform) and m.p. 133°.

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[1] For a review of the mechanisms of this reaction see A. Schönberg and R. Moubasher, *Chem. Revs.*, **50**, 261 (1952).

[2] J. P. Greenstein, L. Levintow, C. G. Baker and J. White, *J. Biol. Chem.*, **188**, 647 (1951).

pounds is greater than that of those previously reported. The observed melting points of the optically active derivatives are also somewhat higher than the literature values. A mixture of the *d*- and *l*-forms recrystallized from ethanol gave α-methylbutyraldehyde 2,4-dinitrophenylhydrazone with a melting point in good agreement with those reported for the racemic compound.

Experimental[3]

Degradation of L-Isoleucine to *d*-α-Methylbutyraldehyde 2,4-Dinitrophenylhydrazone.—In a 200-ml. steam distillation flask there was placed a solution of 0.26 g. of L-isoleucine in 20 ml. of water, and steam was introduced until boiling started. To the hot solution there was added 1.5 g. of ninhydrin in 20 ml. of water. The mixture was steam distilled and the vapor was passed into 0.36 g. of 2,4-dinitrophenylhydrazine in 300 ml. of 2 *N* hydrochloric acid. The precipitate was collected by filtration and washed well with water. There was thus obtained 0.44 g. (84%) of derivative, m.p. 132–135°, which upon recrystallization from ethanol yielded 0.35 g. (67%) of *d*-α-methylbutyraldehyde 2,4-dinitrophenylhydrazone, m.p. 135–137°, $[\alpha]_D$ +29.5°, *c* 1 in acetic acid. *Anal.*[4] Calcd. for $C_{11}H_{13}O_4N_4$; C, 49.8; H, 4.9; N, 21.1. Found: C, 49.9; H, 5.2; N, 21.0.

D-Isoleucine as well as L- and D-alloisoleucine were degraded in a similar manner.

Recrystallization of a Mixture of *d*- and *l*-α-Methylbutyraldehyde 2,4-Dinitrophenylhydrazone.—A mixture of 0.055 g. of each of the above isomers was recrystallized from ethanol to yield the racemic compound, m.p. 129–130° (lit. 128–128.5°,[5] 129–130°[6]).

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[3] All m.p.'s are corrected.

[4] Analysis by R. J. Koegel and staff of this Laboratory.

[5] J. D. Roberts and C. Green, THIS JOURNAL, **68**, 214 (1946).

[6] G. Dunn, G. T. Newbold and F. S. Spring, *J. Chem. Soc.*, S 131 (1949).

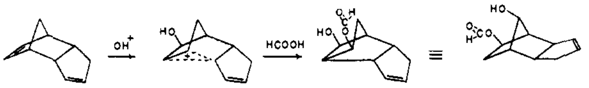
[7] U. S. Public Health Service, Department of Health, Education and Welfare.

The Action of Performic Acid on Dicyclopentadiene[1]

BY MARSHALL GATES AND S. PAUL MALCHICK

RECEIVED AUGUST 19, 1953

We have observed a rearrangement as a result of the action of performic acid[2] on *endo*-dicyclopentadiene which appears to be another example of the well-known[3] *endo–exo* rearrangement occurring in similarly constituted systems. The reaction proceeds readily to yield a glycol monoformate from which a glycol is obtainable on hydrolysis, but this glycol does not react with lead tetraacetate and is inert to periodic acid and is thus clearly not a 1,2-glycol. The following formulation,[1,4] entirely analogous to earlier suggestions,[3] appears plausible.



Cope and co-workers have observed the production of 1,4-cycloöctanediol by the action of performic acid on cycloöctene and by the action of formic acid on cycloöctene oxide,[5] although in this case the product must be produced by a hydride shift rather than by rearrangement of the carbon skeleton.

Experimental

Performic Acid Oxidation.—A well-stirred mixture of 61 g. (0.5 mole) of dicyclopentadiene and 350 cc. of 88% formic acid was cooled in an ice-bath and treated with 68 g. of 25% hydrogen peroxide (0.51 mole). The reaction was allowed to proceed until the mixture became homogeneous, and was then poured into water and extracted twice with ether. The ether layer was washed with bicarbonate, dried and concentrated to leave 58.4 g. of a yellow viscous liquid. Distillation yielded a yellow oil, b.p. 116–123° (0.7–0.8 mm.) whose infrared spectrum contained a prominent carbonyl band at 5.82 μ and a hydroxyl band at 2.92 μ. Five grams of this oil was hydrolyzed with ice-cold 5% aqueous alcoholic potassium hydroxide. After standing 1.5 hours the solution was extracted continuously for 26 hours with methylene chloride. The solvent was removed leaving 4.5 g. of a brown oil, a small amount of which was distilled in a molecular still at 0.03–0.05 mm. (block temperature 120–125°) to give the glycol as a yellow very viscous liquid whose infrared spectrum had lost all but a trace of the carbonyl band at 5.82 μ. The intensity of the hydroxyl band at 2.92 μ had increased.

Anal.[6] Calcd. for $C_{10}H_{14}O_2$: C, 72.31; H, 8.42. Found: C, 71.97; H, 8.01.

Lead Tetraacetate Oxidation.—A solution of 6.45 g. (0.039 mole) of the above glycol and 17.3 g. (0.039 mole) of lead tetraacetate in 35 ml. of glacial acetic acid and 200 ml. of methanol was shaken mechanically until no test could be obtained with starch–potassium iodide indicator. The methanol was removed under reduced pressure and the remaining solution was diluted with bicarbonate solution. The precipitated lead salts were removed and the filtrate was extracted three times with ether. Concentration of the dried extracts yielded 2.3 g. of a yellow liquid which was distilled in a molecular still at 0.03 mm. (block temperature 110°) to give a very viscous yellow oil whose infrared spectrum was identical with that of the starting material.

Periodic Acid Oxidation.—An excess of the above glycol in alcohol was treated with 25 ml. of 0.1532 *N* periodic acid[7] and allowed to stand for 11 hours. The solution was then neutralized with bicarbonate and a borax buffer and excess potassium iodide were added. The liberated iodine required 33.0 cc. of 0.1053 *N* thiosulfate, corresponding to 22.7 cc. (91%) of unused periodic acid.

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[1] Taken from a dissertation presented to the faculty of Arts and Sciences of the University of Rochester in partial fulfillment of the requirements for the degree Doctor of Philosophy.

[2] D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, THIS JOURNAL, **67**, 1786 (1945).

[3] P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946); R. B. Woodward and H. Baer, *ibid.*, **70**, 1161 (1948); see also S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952), and P. D. Bartlett, Abstracts, Twelfth National Organic Chemistry Symposium, Denver, Colorado, 1951, p. 1.

[4] The stereochemistry illustrated for the two substituents follows from the initially preferred *exo* addition of the OH+ entity after which the reaction of the ion with formate ion or formic acid at the side opposite the unsaturated five-membered rings yields the configuration given.

[5] A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952).

[6] Analysis by Mme. Odette Sauvage.

[7] Prepared according to H. H. Willard and C. H. Greathouse, THIS JOURNAL, **60**, 2869 (1938).

The β-Nitration of 2-Thenaldehyde

BY WILLIAM O. FOYE, JOHN J. HEFFERREN AND EDWARD G. FELDMANN

RECEIVED OCTOBER 19, 1953

Recent activity in the preparation and biologic testing of nitroaldehyde derivatives has provided a number of compounds that have anti-viral activity, such as 5-nitro-2-furaldehyde semicarbazone[1]

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[1] M. D. Eaton, M. E. Perry and I. M. Gocke, *Proc. Soc. Exptl. Biol. Med.*, **77**, 422 (1951).