

and does not appear to have been investigated in the case of simple alcohols to which we confined our present study.

Whether the olefins obtained by our method from several representative primary alcohols have a double bond in the 1,2- or 2,3-position or are mixtures of the two isomers has not as yet been established with certainty by us because of the difficulties involved in such a study.

In a typical example 130 g. (1 mole) of *n*-octanol and 62 g. (1 mole) of boric acid were gradually heated to 350°. Water was continuously separated from the azeotrope which distilled over, the alcohol being returned to the reaction mixture. After the removal of one mole of water there began the distillation of octene and water. When the distillation stopped a second mole of *n*-octanol was added to the residue and the operation repeated. The combined distillates from three moles of *n*-octanol were dried over sodium sulfate and redistilled; yield 300–305 g. (90%), b. p. 120–124° (lit. b. p. for octene-1 122°, for octene-2 124–125°).

The following alcohols were converted at 350° into the corresponding olefins with yields of 85–95%: *n*-hexanol, 2-ethylhexanol, *n*-heptanol, *n*-octanol, octanol-2 and cyclohexanol. In the case of 1-phenylethyl alcohol the yield was 50% due to the partial polymerization of styrene produced. The products were identified by their boiling point, specific gravity, bromine number and the m. p. of the dibromide in the case of styrene.

The scope and limitations of this method remain to be determined.

GALAT CHEMICAL CORPORATION
61 SOUTH BROADWAY
YONKERS, N. Y.

RECEIVED JANUARY 19, 1950

2-Methylpentyl Trifluoroacetate

BY EDWARD E. BURGOYNE AND FRANCIS E. CONDON

Direct esterification of trifluoroacetic acid with some alcohols presents uncommon experimental difficulties. For example, the boiling points of alcohol and ester may be similar, and the two may form an azeotrope, making undesirable the use of an excess of alcohol. The alternative, use of an excess of trifluoroacetic acid, is impracticable or undesirable not only for reasons of economy but also because separation of the excess acid by fractional distillation would be accompanied by excessive trifluoroacetic acid-catalyzed hydrolysis of the ester, inasmuch as the acid forms a maximum-boiling azeotrope with water¹; removal of excess acid by extraction with dilute alkali is to be avoided because of the ease of alkaline hydrolysis of esters of fluoro acids.²

In the present work, 2-methylpentyl trifluoroacetate was prepared from approximately equimolar quantities of trifluoroacetic acid and 2-methyl-1-pentanol, without a catalyst, by the use of chloroform for azeotropic removal of the water of esterification.³

(1) Swarts, *Bull. sci. acad. roy. Belg.*, **8**, 343 (1922); *C. A.*, **17**, 769 (1923).

(2) "Heptafluorobutyric Acid," Minnesota Mining and Manufacturing Co., St. Paul, Minn., p. 5.

(3) Cf., for example, Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, pp. 64–66.

Within limitations imposed by the alcohol, the method appears generally applicable to the esterification of fluoroacids. It was successful for the esterification of heptafluorobutyric acid with ethanol; but not with 2,2,3,3,4,4,4-heptafluoro-1-butanol.

Experimental Part

2-Methylpentyl Trifluoroacetate.—One side arm of a 500-ml. three-necked flask was fitted with a 25 cm. × 2 cm. column packed with ³/₁₆-in. (about 5 mm.) glass helices, and having a total condensation-partial takeoff head, which communicated with the top of a vented graduated 100-ml. separatory funnel, whose stem passed into the flask through the other side arm. In the flask were placed 80.5 g. (0.71 mole) of trifluoroacetic acid (Minnesota Mining and Manufacturing Co., St. Paul), 56.0 g. (0.55 mole) of 2-methyl-1-pentanol (Eastman Kodak Co., Practical Grade), and about 100 ml. of chloroform. No catalyst was used. The center outlet of the flask was corked, and distillation of the mixture was begun. The distillate separated into two layers, and the lower layer was periodically returned to the flask through the stopcock on the separatory funnel. When the upper layer measured 20 ml., representing approximately the theoretical amount of water plus the excess trifluoroacetic acid, most of the chloroform was distilled without being returned to the flask. The residue was distilled through the column. There was obtained 98.5 g. (91%) of 2-methylpentyl trifluoroacetate distilling at 138–142°; *n*_D²⁰ 1.3625; *d*₄²⁰ 1.0504 g./cc. (by Mr. L. Swander). Molecular refractivity calcd. for 2-methylpentyl trifluoroacetate, 41.3 cc.; found, 41.9 cc. (In calculating the molecular refractivity, bond refractivities given by Denbigh⁴ were used, except that the C–F bond refractivity was evaluated as 1.82 cc. from known constants for octadecafluoro-*n*-butyl ether.) Saponification equivalent calcd. for 2-methylpentyl trifluoroacetate, 198.2; found (by Miss Dorothy Carter), 206, 203. *Anal.* Calcd. for C₈H₁₃O₂F₃: F, 28.8. Found (by Mr. B. B. Buchanan): F, 28.2, 27.3.

(4) Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

PHILLIPS PETROLEUM COMPANY
RESEARCH DEPARTMENT

BARTLESVILLE, OKLAHOMA RECEIVED MARCH 31, 1950

The Ultraviolet Absorption Spectra of Certain Organosilicon Compounds

BY CHARLES A. BURKHARD AND EARL H. WINSLOW

Recently it was necessary to determine the ultraviolet absorption spectra for several types of organosilicon compounds. Inasmuch as very few ultraviolet absorption spectra data are available in the literature for these compounds it was thought worthwhile to publish such data at this time. Bowden, Boude and Jones¹ have reported ultraviolet absorption data for 3-methyl-1-triethylsilylpent-3-en-1-yne in *n*-hexane (λ_{\max} 234 m μ). This compound differs from the compounds we have investigated in that all of our compounds were of the siloxane type.

We have obtained ultraviolet absorption spectra data for isoöctane² solutions of 1,3-diphenyltetramethyldisiloxane, 2,2-diphenylhexamethyltrisiloxane, *cis*-1,3,5-triphenyltrimethylcyclotrisiloxane and a methyl phenyl silicone oil (20 mole %

(1) Bowden, Boude and Jones, *J. Chem. Soc.*, 948 (1946).

(2) Phillips Petroleum Company "Spectro Grade" Isoöctane was used in this work.