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.

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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 water[1]; 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]

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°; $n^{20}\text{D}$ 1.3625; d^{20} 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 Denbigh[4] 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 $C_8H_{13}O_2F_3$: F, 28.8. Found (by Mr. B. B. Buchanan): F, 28.2, 27.3.

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(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.

(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 Jones[1] have reported ultraviolet absorption data for 3-methyl-1-triethylsilylpent-3-en-1-yne in *n*-hexane ($\lambda_{\text{max.}}$ 234 mμ). 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 isoöctane[2] solutions of 1,3-diphenyltetramethyldisiloxane, 2,2 - diphenylhexamethyltrisiloxane, *cis*-1,3,5-triphenyltrimethylcyclotrisiloxane and a methyl phenyl silicone oil (20 mole %

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

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

phenyl) by use of 1-cm. cells in the Carey Recording Spectrophotometer. It is noted that the wave lengths of absorption maxima are quite similar for these four compounds and in addition that 1,3-diphenyltetramethyldisiloxane alone has prominent absorption peaks at 247.5 and 265.5 mμ. Table I contains a tabulation of the wave lengths of the absorption maxima for these four compounds.

TABLE I

ABSORPTION MAXIMA FOR PHENYL-CONTAINING SILICONES

	Compound	Wave length of absorption maxima, mμ					
a	1,3-Diphenyltetramethyldisiloxane	247.5	253	259	263	265.5	270
b	2,2-Diphenylhexamethyldisiloxane	248	253	259	263	265	270
c	*cis*-1,3,5-Triphenyltrimethylcyclotrisiloxane	248	253	259	263	270	
d	General Electric Co. methyl phenyl silicone oil	248	253	259	263	270	

Although it was possible to obtain Beer's law plots for isoöctane solutions of any one of these compounds, the quantitative determination of phenyl content by comparison of the absorbency of one compound with that of another, taken as a standard, was unsuccessful. No attempt was made to study the effect of siloxane structure or composition upon these ultraviolet absorption spectra (*e. g.*, the effect of varying the number of phenyl groups per silicon atom).

In addition to the curves obtained for the isoöctane solutions of these phenyl-containing compounds, ultraviolet absorption spectra were obtained also for the following undiluted compounds in 2-cm. cells: hexamethyldisiloxane, octamethylcyclotetrasiloxane, and a linear methylsilicone oil.[3] Table II contains a tabulation of the wave lengths of the absorption peaks for these non-phenyl-containing organosilicon compounds.

TABLE II

ABSORPTION MAXIMA FOR NON-PHENYL-CONTAINING SILICONES

	Compound	Approximate wave length of prominent absorption maxima (mμ)					
a	Hexamethyldisiloxane	247	252	259	261	265	268
b	General Electric Co. 9981-LTNV-40 methyl silicone oil	252	258	261	269		
c	Octamethylcyclotetrasiloxane	246	252	260	268		

The apparent similarity between the absorption curves for the undiluted General Electric 9981-LTNV-40 methyl silicone oil and octamethylcyclotetrasiloxane and the curves obtained for the isoöctane solutions of phenyl-containing silicones would indicate that a phenyl bonded to silicon grouping is present as an impurity. However, the methods of preparation of these materials and the intermediates that are used seemingly preclude the presence of an impurity of this type. A comparison of these absorption curves with those of possible non-silicone impurities does not exclude the presence of a hydrocarbon such as benzene.[4] However, by diluting General Electric 9981-LTNV-40 methylsilicone oil with isoöctane a solution is obtained, the absorption curve of which is coincident with that of the isoöctane blank. This then indicates that if an impurity of either the phenyl silicone or aromatic hydrocarbon type is present, it is present in trace amounts only.

The authors wish to acknowledge the assistance given by Dr. H. W. Alter of the Knolls Atomic Power Laboratory in obtaining the Carey instrument curves.

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[3] General Electric Company 9981-LTNV-40 silicone oil.

[4] Tunnicliff, Brattain and Zumwalt, *Anal. Chem.*, **21**, 890 (1949).

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, N. Y.

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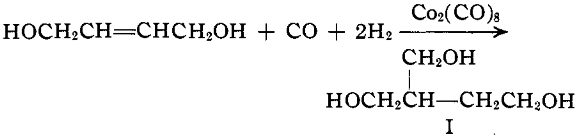
Application of the Oxo Reaction to 2-Butene-1,4-diol

BY L. E. CRAIG, R. M. ELOFSON AND I. J. RESSA

The "oxo" reaction was applied to 2-butene-1,4-diol in hopes of producing a triol (I)



$$\mathrm{HOCH_2CH{=}CHCH_2OH + CO + 2H_2 \xrightarrow{Co_2(CO)_8} HOCH_2\overset{\displaystyle CH_2OH}{\overset{|}{C}}H{-}CH_2CH_2OH}$$

I

However, the main product of the reaction was found to be a rather low boiling alcohol and was presumed to be 3-tetrahydrofurfuryl alcohol formed by the splitting-out of a molecule of water from I. However, the preparation of derivatives of the product suggested that it was 2-tetrahydrofurfuryl alcohol. This was confirmed by mixture melting points of the derivatives with those of an authentic sample of 2-tetrahydrofurfuryl alcohol and by a comparison of the infrared absorption curves of the product and the known alcohol (Fig. 1).

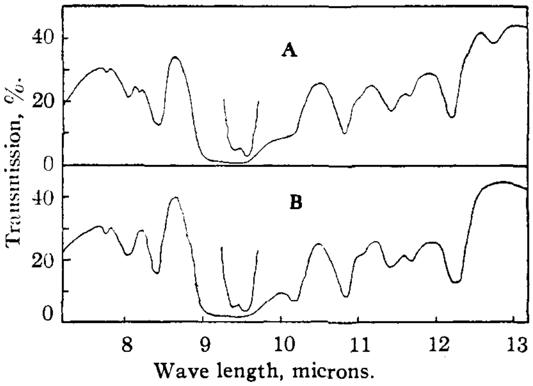


Fig. 1.—Curve A, absorption spectrum of the product of the oxo reaction with 2-butene-1,4-diol; curve B, absorption spectrum of 2-tetrahydrofurfuryl alcohol.