physical constants were in good agreement with those recorded previously.[3] Acetylation gave the corresponding acetate, m. p. 115–116°,[5] for which the specific rotation of −61° (in chloroform) was claimed. According to standard tables[6] allopregnan-3β-ol and its acetate would be expected to have specific rotations of +16 and +6°, respectively. Since Huang-Minlon's recorded rotation of −61° was so different from the expected value and since these are compounds in which "vicinal action" would not be anticipated[7] to invalidate the comparison of molecular rotations, it seemed to us to be worthwhile to reinvestigate the properties of allopregnan-3β-ol and its derivatives. For the acetate of allopregnan-3β-ol we now find, m. p. 113–114°, $[\alpha]_D$ +5° (in chloroform).[8] A summary of the molecular rotations of allopregnan-3β-ol derivatives given in the Table shows that the values are in excellent agreement with those found in the cholestane series. The replacement of the saturated isoöctyl side chain of cholestanol by an ethyl group causes no "vicinal action" at the 3-position.

TABLE I

$[M]_D$ (in chloroform)

Substance	Alcohol	Acetate	Benzoate	Ketone	Δ_1[a]	Δ_2	Δ_3
Cholestan-3β-ol[b]	+ 89	+ 60	+ 94	+162	−29	+5	+73
Allopregnan-3β-ol	+ 48	+ 17	+ 49	+120	−31	+1	+72
Δ^5-Pregnen-3β-ol[c]	−181	−214	−105	+331			
Δ[d]	+229	+231	+154	−211			
Compare standard Δ values[e]	+243	+248	+168	−195			

[a] Δ_1 is the increment in molecular rotation on acetylation, Δ_2 that on benzoylation and Δ_3 that on oxidation to the ketone. [b] Barton, *J. Chem. Soc.*, 1116 (1946). [c] Barton, Holness and Klyne, *ibid.*, 2456 (1949). [d] Difference in molecular rotation on saturation of the Δ^5-ethylenic linkage. [e] From the cholesterol-cholestanol series; see Barton and Cox, *ibid.*, 783 (1948).

Experimental[9]

The standard chemical operations of acetylation, benzoylation, alkaline hydrolysis, etc., were carried out as detailed previously.[10]

Allopregnan-3β-yl Acetate.—This compound was prepared by the hydrogenation of Δ^5-pregnen-3β-yl acetate (from 600 mg. of Δ^5-pregnen-3β-ol-20-one acetate)[11] in 25 ml. of acetic acid at room temperature using 100 mg. of platinum oxide catalyst. After working up in the usual manner the product was chromatographed over alumina (Savory and Moore's standardized) to give six fractions m. p.'s 105–110°, 107–111°, 110–112°, 109–111°, 111–113° and 110–113°. The last five were recrystallized three times from chloroform–methanol to give 405 mg. of pure allopregnan-3β-yl acetate, m. p. 113–114°, $[\alpha]_D$ + 5° (*c*, 2.28), + 6° (*c*, 1.40).

Allopregnan-3β-ol and Derivatives.—Alkaline hydrolysis of allopregnan-3β-yl acetate afforded allopregnan-3β-ol, recrystallized from methanol, m. p. 135–137°, $[\alpha]_D$ + 16° (*c*, 3.15). Benzoylation of the latter furnished allopregnan-3β-yl benzoate, recrystallized from chloroform–methanol, m. p. 154–155°, $[\alpha]_D$ + 12° (*c*, 1.67).

Anal. Calcd. for $C_{28}H_{40}O_2$: C, 82.28; H, 9.91. Found: C, 82.25; H, 9.8.

Chromic acid oxidation of allopregnan-3β-ol and chromatography over alumina (Savory and Moore's standardized) gave allopregnan-3-one, recrystallized from methanol, m. p. 112–113°, $[\alpha]_D$ + 39° (*c*, 0.91).[12]

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[3] (a) Ruzicka, Meister and Prelog[4a] gave m. p. 137–138°, $[\alpha]_D$ +18°. (b) Ruzicka, Goldberg and Hardegger[4b] found m. p. 137–138°, $[\alpha]_D$ +16°. Both rotations in chloroform.

[4] (a) Ruzicka, Meister and Prelog, *Helv. Chim. Acta*, **30**, 867 (1947); (b) **22**, 1294 (1939).

[5] Ruzicka, Goldberg and Hardegger[4b] found m. p. 115–116°. The rotation was not recorded.

[6] Barton and Klyne, *Chem. and Ind.*, 755 (1948).

[7] Barton and Cox, *Nature*, **159**, 470 (1947); *J. Chem. Soc.*, 783 (1948); Barton, *Angew. Chem.*, **61**, 57 (1949).

[8] The m. p. is in agreement with previous workers[2,5] and there seems no reason to doubt the purity of Huang-Minlon's preparation.

[9] M. p.'s are not corrected. All specimens were dried *in vacuo* at 20° below their m. p.'s or at 120°, whichever was the lower temperature, before taking the rotation. All rotations are for the sodium D line and in chloroform solution. The measurements were made at room temperature which varied from 15 to 25°. All values of $[\alpha]_D$ have been approximated to the nearest degree. Concentrations (*c*) are expressed in g. per 100 ml.

[10] Barton and Cox, *J. Chem. Soc.*, 783 (1948).

[11] Barton, Holness and Klyne, *ibid.*, 2456 (1949).

[12] Ruzicka, Meister and Prelog[4a] found m. p. 116–118°, $[\alpha]_D$ +44° (in chloroform). Ruzicka, Goldberg and Hardegger[4b] gave m. p. 116–117°.

Olefins from Alcohols

BY WALTER BRANDENBERG AND ALEXANDER GALAT

The conversion of alcohols into olefins, one of the fundamental operations in organic chemistry, can be accomplished by several well-known methods. However, the dehydration of primary alcohols is invariably difficult except in the case of the low-molecular aliphatic alcohols. No general method is known which would accomplish this conversion in good yield.

We wish to record a new method for the preparation of olefins from alcohols which effects this conversion in excellent yields by the use of a mild catalyst and is applicable to primary alcohols, as well as secondary and tertiary. We have found that the dehydration of alcohols can be effected almost quantitatively by the use of boric acid or anhydride as catalyst. The study of the mechanism of this reaction showed that it involves two steps: (1) the formation of the boric ester and (2) the decomposition of the boric ester into the olefin with the regeneration of the catalyst

$$3R{-}CH_2CH_2OH + H_3BO_3 \longrightarrow B(OCH_2CH_2R)_3 \longrightarrow 3R{-}CH{=}CH_2 + H_3BO_3$$

The new method is thus similar to the one involving the pyrolysis of acetates[1] except that the reaction proceeds at much lower temperatures and is of a true catalytic character. However, a comparison of the two methods is not possible at this time since the pyrolysis of the acetates has been applied only to a few rather special cases

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[1] Frank, Berry and Shotwell, THIS JOURNAL, **71**, 3889 (1949); Burns, Jones and Richie, *J. Chem. Soc.*, 400 (1935); Schniepp and Geller, THIS JOURNAL, **67**, 54 (1945); Ratchford and Fisher, *ibid.*, **69**, 1911 (1947).

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.

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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}_{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).

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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 ($\lambda_{\max}$ 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.