hydrous potassium fluoride has been described recently.[1,2,3] Since this reaction takes place only at higher temperatures, the use of pressure equipment is required and much trouble is due to coating of potassium fluoride with potassium chloride or potassium bromide, respectively. Only in the special case of the preparation of fluoroacetamide from chloroacetamide the use of xylene as reaction medium allows the reaction to be carried out at atmospheric pressure.[3]

By using suitable organic solvents for anhydrous potassium fluoride, it is possible to exchange the halogens in —CHX— and —CH$_2$X groups (X = Cl, Br, I) in a one-step reaction at atmospheric pressure in ordinary glass equipment. In order to obtain reasonably fast reaction rates, the method requires a temperature of about 140° and over, so that low-boiling solvents for potassium fluoride, such as methanol and ethanol cannot be used. Satisfactory solvents are aliphatic di- and polyhydroxy compounds such as ethylene glycol, glycerol, diethylene glycol, polyethylene glycol, etc., either singly or mixed.

In this procedure the yields are fair and frequently considerably higher than those obtained by the pressure method. *n*-Hexyl fluoride can thus be obtained from *n*-hexyl chloride in 54% yield, whereas the halogen exchange under pressure without solvent for the potassium fluoride gives only a 20% yield.[2] 2-Fluoroethanol, which could not be obtained by heating of ethylene chlorohydrin with potassium fluoride under pressure by Gryszkiewicz-Trochimowski[4], was, however, prepared by McCombie and Saunders[1] by the same method at 135–140° (no yield indicated). The subject method permits the preparation of this compound in 42.5% yield by using potassium fluoride in a glycol solvent at atmospheric pressure. Another advantage of the use of a solvent for the halogen exchange is the fact that the presence of small amounts of moisture in one of the reactants can lead to serious hazards by enormous pressure increase in the conventional method,[2] whereas in the described method only the yield of fluorinated product is correspondingly decreased.

Although the subject method is in some respects inferior to conventional methods using fluorides of mercury, etc., the ready availability of the inexpensive potassium fluoride makes it another convenient means for the preparation of aliphatic fluorides, especially since some fluorides such as 2-fluoroethanol, β-difluoroethyl ether, etc., which cannot be obtained by fluorination with silver or mercuric fluoride, are accessible from the corresponding chlorine compounds by fluorination with potassium fluoride.

A large number of new aliphatic fluorine compounds was synthesized by this method by the writer in collaboration with R. Geier in the laboratories of W. Bockemüller in Würzburg, Germany.

The syntheses of 2-fluoroethanol and *n*-hexyl fluoride from the corresponding chlorine compounds by halogen exchange with anhydrous potassium fluoride in glycol solution are described in detail in the following.

Preparation of FCH$_2$CH$_2$OH.—A mixture of dry, powdered potassium fluoride (350 g., 6 moles), ethylene glycol (320 g.), and diethylene glycol (130 g.) was heated to 170° in a 3-neck, 1-liter, round-bottom flask fitted with a stirrer, dropping funnel, and a 30-cm., 3-step Vigreux column with attached condenser and receiver. Ethylene chlorohydrin (322 g., 4 moles) was added dropwise in the course of three hours to the reaction mixture maintained at 170–180° with constant stirring at such a rate that the distillate at the still head showed a temperature of 95–105°. After addition of ethylene chlorohydrin was complete, a slow stream of air was sucked through the apparatus for one hour in order to distil off the fluoroethanol completely. In the receiver, 152.5 g. of crude reaction product was obtained as a colorless liquid. After standing with 10 g. of sodium fluoride for two days to remove traces of hydrogen fluoride, distillation of the reaction product yielded 109 g. (42.5%) of fluoroethanol (b. p. 101°,[1] 100–102°[2]) between 97° and 104°.

Preparation of CH$_3$(CH$_2$)$_4$CH$_2$F.—A mixture of dry, powdered potassium fluoride (116 g., 2 moles), ethylene glycol (200 g.), and diethylene glycol (50 g.) was heated to 180° in a 3-neck, 1-liter, round-bottom flask fitted with a stirrer, dropping funnel and a 30-cm., 3-step Vigreux column with attached condenser and receiver. *n*-Hexyl chloride (120.6 g., 1 mole) was added dropwise in the course of eight hours to the reaction mixture maintained at 175–185° with constant stirring. Since the reaction product boils at 93.2°, it distils out of the reaction mixture at about the same rate at which the reagent is added. After addition of hexyl chloride was complete, the reaction mixture was allowed to cool to 110°. A slow stream of air was sucked through the apparatus in order to distil off the remaining reaction product from the mixture. In the receiver, 79.6 g. of distillate was collected. This consisted of *n*-hexyl fluoride with some hexene and some unreacted hexyl chloride. Fractionation yielded 56.3 g. (54.1%) of *n*-hexyl fluoride, boiling at 91–93.5°.

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(1) McCombie and Saunders, *Nature*, **158**, 382 (1946).

(2) Gryszkiewicz-Trochimowski, Sporzyński and Wnuk, *Rec. trav. chim.*, **66**, 413–418 (1947).

(3) Bradley, U. S. Patent 2,403,576 (July 9, 1946).

(4) Gryszkiewicz-Trochimowski, *Rec. trav. chim.*, **66**, 427 (1947).

The Terpenes of Oil Sweet Goldenrod

BY BRYANT R. HOLLAND

In a study of the production of essential oils, oil of Sweet Goldenrod (*Solidago odora*)[1] has been investigated. Miller and Moseley[2] examined this oil fairly extensively, but did not identify the terpenes. They identified methyl chavicol as the main constituent, and showed borneol to be present. To extend the findings of Miller and Moseley, the oil has been partially fractionated and the terpenes determined.

Experimental

A 600-ml. sample of fresh oil was fractionated using a Stedman column (24 inch packing, 1 inch diameter) at a pressure of 5 mm. with a reflux ratio of 0.5 (50% of the condensate returned to the column). The starch–glycerol

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(1) The complete investigation is to be reported in a Texas Engineering Experiment Station Bulletin.

(2) Miller and Moseley, THIS JOURNAL, **37**, 1285 (1915).

stopcock lubricant described by Herrington and Starr[3] was a satisfactory lubricant for the stopcocks and ground joints used in the distillation apparatus. The following fractions were obtained:

Fraction	Volume, ml.	Temp., °C.	$n^{29}\text{D}$	$\alpha^{29}\text{D}$
1	20	30	1.4677	+84.17°
2	60	31	1.4683	+96.67°
3	10	32	1.4690	+92.00°
Residue	510	..	1.5173	− 0.50°

Fractions 1, 2 and 3 account for 15% of the oil. The physical properties of fraction 2 are similar to those of *d*-limonene. The presence of *d*-limonene was confirmed by preparing the β-nitrol anilide, m. p. 153°, and the tetrabromide, m. p. 103.5°, $[\alpha]^{30}\text{D}$ +72.0° (0.1785 g. of *d*-limonene tetrabromide in 5 ml. of carbon tetrachloride solution).

A 1500-ml. portion of the fresh oil was subsequently fractionated, as above, at a pressure of 22 mm., with a reflux ratio of 0.9 (90% of the condensate returned to the column). The first fraction, 3.1 ml., boiling at 55°, had a refractive index of 1.4628^{25}, and a rotation of −37.67°. Calculated for *l*-α-pinene this would be a specific rotation of −43.70°, which is near the reported −48.63°.[4] The presence of *l*-α-pinene was confirmed by the preparation of α-pinene nitrolpiperidine, m. p. 118.5°. The quantity found by distillation represents 0.2% of the oil.

The specific rotation of *d*-limonene as calculated from the rotation of fraction 2 would be +114°, as compared to a specific rotation for pure *d*-limonene of +126°.[5] This plus the refractive index of fraction 2 indicates the probable presence of dipentene. No direct evidence for the presence of dipentene or other terpenes was obtained. The negative rotation of the terpeneless residue indicates that the borneol is probably *l*-borneol. Methylchavicol, an isomer of anethol, is responsible for the anise-like odor and flavor. The odor and flavor of the oil are decidedly improved by the removal of the terpenes.

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[3] Herrington and Starr, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 62 (1942).

[4] Gildemeister and Hoffmann, "The Volatile Oils," second edition, John Wiley and Sons, Inc., New York, N. Y., 1913, Vol. I, p. 293.

[5] Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 575.

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Preparation of Tetraacetyl-α-D-glucopyranosyl Bromide

BY C. G. JEREMIAS, G. B. LUCAS AND C. A. MACKENZIE

There are many references in the literature pertaining to the preparation of tetraacetyl-α-D-glucopyranosyl bromide. Most authors recommend the use of an acetic acid solution of hydrogen bromide with pentaacetyl-β-D-glucose. They differ in their experimental details, particularly with respect to the use of vacuum distillations, solvents and purifications methods. The description given below eliminates vacuum distillations, simplifies the purification process and gives a pure product in good yield with a minimum of effort.

Experimental

A mixture of 20 g. of pentaacetyl-β-D-glucose and 20 ml. of hydrobromic acid–acetic acid solution (Eastman Kodak Co. 30–32% hydrobromic acid–acetic acid) is stirred at room temperature for two hours in a flask protected from moisture. The clear, yellow solution is poured, in a thin stream, into 400 ml. of vigorously stirred ice water. A finely divided, crystalline material is obtained. If the addition is made too rapidly the product solidifies in the form of large lumps. The crude acetobromoglucose is filtered with suction and then transferred to a small separatory funnel. Fifty ml. of carbon tetrachloride is added to put the solid into solution. The water layer formed is drawn off with a suction pipet and the product remaining is washed once with 20 ml. of ice water and then with a few ml. of cold, saturated sodium bicarbonate solution until all free acid has been removed. The solution is finally washed with two 20-ml. portions of ice water. The carbon tetrachloride layer is filtered through glass wool into an erlenmeyer flask and dried over calcium chloride. The dry solution is poured slowly, with stirring, into 200 ml. of petroleum ether (35–75° boiling range was used; a good quality reagent is necessary or a yellowing of the product may occur at this point). When crystallization at room temperature is complete, an ice-salt-bath is placed around the container and an additional crop of crystals form. The crystals are filtered with suction and air-dried or dried in a vacuum desiccator. The product at this point has a m. p. 88–89°; yield, about 18 g. (80–85%).

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Heats of Mixing of Some Fluorinated Ethers with Chloroform

BY J. R. LACHER, J. J. MCKINLEY AND J. D. PARK

It is well known that chloroform and monofluorodichloromethane will form hydrogen bonds with solvents containing donor atoms such as nitrogen and oxygen.[1] Diethyl ether[2] and polyethylene glycol ethers[3] show a considerable heat evolution when mixed with chloroform or monofluorodichloromethane. The substitution of chlorine in an aliphatic ether[4] or the replacing of an alkyl by an aryl group[5] reduces considerably the tendency for bonding. Recently[6] a number of polyfluoro alkyl ethers have been prepared in this Laboratory. If one interprets hydrogen bonds as the result of an interaction between dipoles,[7,8,9] one might expect that these fluorinated ethers would also show only a slight tendency for hydrogen bonding. The moments are not known for these molecules. However, one can calculate,

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[1] C. S. Marvel, M. J. Copley and E. Ginsberg, THIS JOURNAL, **62**, 3263 (1940). This paper gives references to earlier work by these and other authors.

[2] D. B. McLeod and F. J. Wilson, *Trans. Faraday Soc.*, **31**, 598 (1935).

[3] G. F. Zellhoefer and M. J. Copley, THIS JOURNAL, **60**, 1343 (1938).

[4] G. F. Zellhoefer, M. J. Copley and C. S. Marvel, *ibid.*, **60**, 1337 (1938).

[5] C. S. Marvel, M. J. Copley and E. Ginsberg, *ibid.*, **62**, 3109 (1940).

[6] J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, THIS JOURNAL, **70**, 1550 (1948).

[7] G. Briegleb, *Z. Elektrochem.*, **50**, 35 (1944).

[8] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944.

[9] G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944.