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}D	α^{29}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°, $[\alpha]^{30}$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.

TEXAS ENGINEERING EXPERIMENT STATION
AGRICULTURAL AND MECHANICAL COLLEGE OF TEXAS
COLLEGE STATION, TEXAS
RECEIVED FEBRUARY 20, 1948

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%).

RICHARDSON CHEMISTRY LABORATORIES
DEPARTMENT OF CHEMISTRY
THE TULANE UNIVERSITY OF LOUISIANA
NEW ORLEANS, LOUISIANA
RECEIVED APRIL 9, 1948

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.

using bond moments,[10] the dipoles for similar compounds. Dimethyl ether has a moment of 1.32 debye units and the negative end may be regarded as being on the oxygen atom. Hexafluorodimethyl ether, on the other hand, has a calculated dipole moment of 0.40 debye unit and the direction of the moment is reversed. Methyl trifluoromethyl ether has a calculated moment of 1.31 and it makes an angle of 37° with the methyl–oxygen bond. Its negative end lies between the oxygen and the trifluoromethyl group. As a result the negative charge is spread out between the two. A similar situation will obtain for the ethers dealt with here. Experiments were undertaken to measure their hydrogen bonding tendencies and the method chosen involves measuring their heats of mixing with chloroform at 0°.

The mixing calorimeter was modified after those described by McLeod and Wilson,[2] Vold,[11] Von Steinwehr,[12] and Zellhoefer and Copley.[4] The mixing chamber consisted of a 170-cc. Pyrex dewar which could be evacuated by means of a diffusion pump. A tight fitting lid contained holes to receive two pipets and a long Pyrex tube. The latter contained a 12-junction copper–constantan thermocouple, nichrome heater, and also served as a stirrer. The lower end of the tube was fitted with a glass disk and stirring was accomplished by means of a reciprocating motor. The whole assembly was contained in a gallon dewar and maintained at 0° with ice. The output from the thermel was fed into a Leeds–Northrup "Speedomax" recorder. In making a run, the temperature change produced on mixing two liquids was compared with that produced by electrical heating in the usual way.

The preparation of the fluoroalkyl ethers has been previously described.[6] Diethyl ether was dried over sodium and distilled. Acetone was purified by the method of Shipsey and Werner[13] using sodium iodide. Monofluorodichloromethane, furnished us through the courtesy of Mr. A. F. Benning of the du Pont Company, was distilled in a twenty-plate column.

Discussion.—In order to check the reliability of the apparatus and develop the necessary technique, the heats of mixing of chloroform with diethyl ether and with acetone were measured. The former system has been studied by McLeod and Wilson[2] at 0° and the latter by Hirobe[14] at 25°. The data obtained are shown in Figs. 1 and 2. The heat evolved in calories per mole of solution may be represented by a parabolic curve of the type: $-\Delta H = (N - N^2)A$. N represents the mole fraction of the halogenated hydrocarbon and A is an adjustable constant. These curves, also shown in the figures, give heats of mixing of −670 and −470 cal./mole for diethyl ether and acetone, respectively, at $N = 0.5$. This compares with −714 and −460 cal./mole determined by McLeod and Wilson and by Hirobe, respectively.

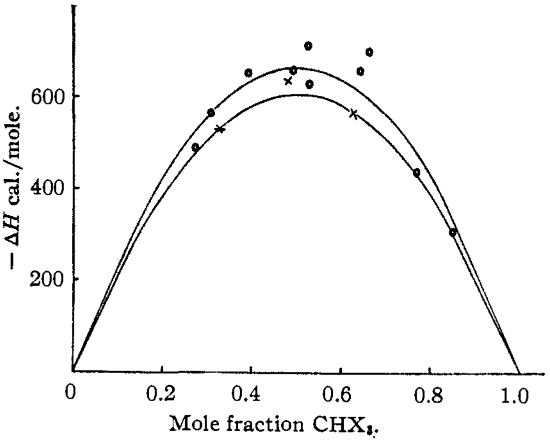

Fig. 1.—Heats of mixing in calories per mole of solution—systems: diethyl ether–chloroform, O, and diethyl ether–$CHFCl_2$, X.

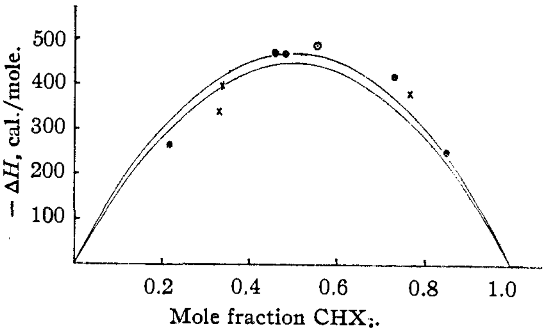

Fig. 2.—Heats of mixing in calories per mole of solution for the systems: O, acetone–chloroform; X, acetone–$CHFCl_2$.

A few runs using monofluorodichloromethane in place of chloroform were made. The results, shown in Figs. 1 and 2, suggest that less heat is liberated when the monofluorinated compound is used. The effect, however, is of the same order of magnitude as the experimental error. Zellhoefer and Copley[3] using polyethylene glycol ethers found a similar situation. The solubility[1] of chloroform in the dimethyl ether of tetraethylene glycol is, however, measurably greater than that of the monofluorinated derivative. This may be interpreted to mean that some C—H ← F bonds were present in $CHFCl_2$. It may also be explained by the fact that, whereas in chloroform the dipole moment is along the carbon–hydrogen bond, in $CHFCl_2$ it is askew. Consequently, a larger decrease in entropy will result when the latter forms a hydrogen bond with the ether. This will account for the larger difference shown between chloroform and $CHFCl_2$ in solubility measurements (which involve a free energy change) than is given in a measurement of ΔH.

[10] C. P. Price, *Chem. Revs.*, **29**, 37 (1941).

[11] R. D. Vold, THIS JOURNAL, **59**, 1515 (1937).

[12] H. Von Steinwehr, *Z. physik. Chem.*, **38**, 139 (1901).

[13] K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

[14] H. J. Hirobe, *Fac. Sci. Imp. Univ., Tokyo*, **1**, 155 (1925).

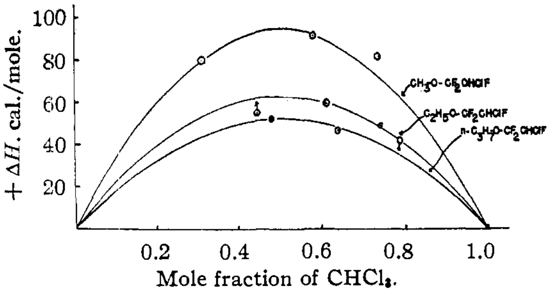

Fig. 3.—Heats of mixing in calories per mole of solution for the systems: chloroform with polyfluoro alkyl ethers.

The results obtained on mixing chloroform with the methyl, ethyl and *n*-propyl derivatives of 1,1,2-trifluoro-2-chloroethyl alkyl ethers are shown in Fig. 3 and Table I gives the heats of mixing per mole of solution at a mole fraction of 0.5.

TABLE I

HEATS OF MIXING OF 1,1,2-TRIFLUORO-2-CHLOROETHYL ALKYL ETHERS WITH CHLOROFORM AT 0°

Ether	ΔH, cal./mole
Methyl	93 ± 3
Ethyl	62 ± 4
n-Propyl	52 ± 3

The isopropyl derivative gave heat effects of the same magnitude as the normal compound. Sufficient material was not on hand for quantitative study. In contrast to the behavior shown by diethyl ether and acetone, the heats of mixing were small and positive. The slight cooling effect produced indicates the lack of formation of hydrogen bonds, at least in large numbers.

UNIVERSITY OF COLORADO
BOULDER, COLORADO
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The Structure of Dioxadiene Dibromide

BY GERALD R. LAPPIN[1] AND R. K. SUMMERBELL

Some time ago dioxadiene was found to react with only one molar equivalent of bromine to give a crystalline compound, dioxadiene dibromide, of unknown structure.[2] This was presumed to be 5,6-dibromo-*p*-dioxene. However, the possibilities that it had an oxonium bromide structure or that the dioxadiene ring had been ruptured were not excluded.

We have now found that I does not react with aqueous potassium iodide solution, a characteristic reaction of oxonium bromides.[3] Furthermore, I reacts with the magnesium–magnesium iodide dehalogenating reagent[2] and with phenylmagnesium bromide to regenerate dioxadiene in high yield. Thus the structure of I must be 5,6-dibromo-*p*-dioxene.

Attempted Reaction of I with Aqueous Potassium Iodide Solution.—To a solution of 1.0 g. of potassium iodide in 20 ml. of water was added 0.5 g. of I. No iodine was liberated on heating at 60° for twenty-four hours.

Reaction of I with Magnesium–Magnesium Iodide Reagent.—In a two-necked flask fitted with a mercury-sealed stirrer and a side-arm connected to a condenser arranged for downward distillation were placed 10 g. of magnesium turnings and 75 ml. of anhydrous butyl ether. To this was added slowly 4 g. of iodine. The solution was heated until distillation started and to it was added dropwise a solution of 10 g. (0.04 mole) of I in 50 ml. of butyl ether. A total of 100 ml. of distillate was collected during this addition. Redistillation through a 10-cm. Vigreux column gave 3.4 g. (97%) of dioxadiene, b. p. 74–75°, $n^{20}D$ 1.4351.

The Reaction of I with Phenylmagnesium Bromide.—To a solution of phenylmagnesium bromide prepared from 2.64 g. (0.11 atom) of magnesium and 17.3 g. (0.11 mole) of bromobenzene in 100 ml. of dry ether was slowly added a solution of 12.3 g. (0.05 mole) of I in 75 ml. of dry ether. After the moderately vigorous reaction subsided the mixture was allowed to stand for twelve hours and was then hydrolyzed by pouring into ice and ammonium chloride solution. The ether solution was separated and dried over magnesium sulfate. Distillation gave 5.9 g., b. p. 75–80°, and a sirupy residue. The distillate was dissolved in 50 ml. of carbon tetrachloride and to it was added dropwise a solution of bromine in carbon tetrachloride at 0° until a faint permanent color remained. Removal of the solvent *in vacuo* gave 9.6 g. of crystalline residue identified as I by mixture melting point. Assuming an average yield of 90% on the addition of bromine to dioxadiene this represents an 87% conversion to dioxadiene.

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS
RECEIVED APRIL 12, 1948

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[1] Present address, Chemistry Department, Antioch College, Yellow Springs, Ohio.

[2] Summerbell and Umhoeffer, THIS JOURNAL, **61**, 3020 (1939).

[3] McIntosh, *ibid.*, **32**, 1330 (1910).

The Solubility of Aluminum Bromide in Cyclohexane[1]

BY PHILIP A. LEIGHTON AND JOHN B. WILKES

During the course of a study of the isomerization of cyclohexane with aluminum bromide catalyst, the solubility of aluminum bromide in cyclohexane has been determined.

Materials.—Aluminum bromide was prepared and distilled into glass ampoules in the manner described by Leighton and Heldman.[2]

The cyclohexane was the gift of the Shell Oil Company. The stated analysis as received was 99.7 vol. % cyclohexane (by correlation of freezing point and mass spectrograph analysis), 0.0003 wt. % sulfur, less than 0.0005 vol. % benzene and less than 0.001 vol. % phenols. The freezing point was 6.0°. This material was further purified by "freezing out" cyclohexane crystals, followed by percolation of the remelted crystals through silica gel. The "freezing out" was performed as follows: About 300 ml. of cyclohexane contained in a 500-ml. Erlenmeyer flask was placed in a cooling bath of ice and water, and, with frequent hand stirring and scraping, a thick slurry of cyclohexane crystals was produced. The crystals were filtered off, melted, and the process repeated. The resultant cyclohexane was percolated through a column of silica gel to remove water and any trace of olefins. The product was stored over sodium in brown glass bottles. Physical properties of the purified cyclohexane were: m. p. 6.5°, $n^{25}D$ 1.4235.

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[1] This work was supported by a grant from the Research Corporation.

[2] Leighton and Heldman, THIS JOURNAL, **65**, 2276 (1943).