solved in carbon disulfide showed a carbonyl absorption band at 1738 kaysers[1] which agrees closely with a literature value[2] of 1740 kaysers for a δ-lactone carbonyl. The spectrum of the lactone fraction showed no absorption band near the higher frequency (1770 kaysers) given in the literature[2] for γ-lactones. On the other hand, authentic samples of γ-stearolactone, γ-valerolactone and γ-butyrolactone showed carbonyl bands at 1784, 1788 and 1786 kaysers, respectively.

Refluxing the lactone with methanol and sulfuric acid as catalyst yielded a derivative, presumably a methyl ester, whose infrared spectrum in carbon disulfide (7.6 g./l.) showed an ester carbonyl absorption band at 1744 kaysers and broad alcoholic hydroxyl absorption bands at 3370 and 3470 kaysers. The total area of these hydroxyl absorptions was appreciably less than that of methyl 12-hydroxystearate, whose major hydroxyl band occurred at 3630 kaysers with minor broad bands at 3370 and 3470 kaysers (8.7 g./l. in CS_2). The original lactone showed no hydroxyl bands.

The ease of δ-lactone formation is well established. From the data obtained it may be inferred that the lactone fraction is a δ-lactone. Such a compound would explain the difficulty encountered in obtaining wool wax acids free of an appreciable saponification number. Furthermore, the above data would indicate the presence of a δ-hydroxy acid in wool wax acids. Thus far the only hydroxy acids isolated from wool wax were α-hydroxy acids.[3-6]

Although the information available indicates the probability that the lactone is a $C_{20}H_{38}O_2$ compound, the data do not eliminate the possibility that we have a difficultly separable mixture of δ-lactones.

Experimental

A 500-g. sample of U.S.P. lanolin was saponified[7] and the resulting mixture was exhaustively extracted with petroleum naphtha (88–98°). From the extract there was isolated 243 g. of material having an acid number of 2.66 and a saponification number of 11.97. The soaps remaining in the lower layer in the continuous extractor were acidified with a 100% excess of concentrated hydrochloric acid and the acid mixture heated for four hours at 68°. The mixture was allowed to cool to room temperature and then continuously extracted with ether for 24 hours. The ether extract was evaporated leaving 261 g. of material having an acid number of 103.5 and a saponification number of 167.5. A 15-g. sample of this material in 30 ml. of reagent grade chloroform was chromatographed on a 4.5 cm. × 39 Florisil column.

The column was developed with petroleum ether (35–60°) (8 liters eluted 10% and an additional 12 liters eluted 2% more by wt.). The residue obtained by evaporating 20 liters of petroleum ether weighed 1.8 g. and contained no free acid.

Anal. Calcd. for $C_{20}H_{38}O_2$: sapn. equiv., 310.5; C, 77.36; H, 12.33. Found: sapn. equiv., 311.1; C, 77.7; H, 12.8; $[\alpha]^{26}D$ +13° (chloroform, $c = 4$); mol. wt. (cryoscopically in benzene), 316.

Methanolysis.—A 0.68-g. sample of lactone was refluxed for 6 hours with 250 ml. of methanol and 2 drops of concentrated sulfuric acid. The reaction mixture was diluted with 200 ml. of water, concentrated to approximately 200 ml. and ether-extracted. The organic layer was washed free of acid with water and then dried over anhydrous granular sodium sulfate. The dry extract was evaporated leaving a residue of 0.78 g., $[\alpha]^{26}D$ +5.0° (chloroform, $c = 1.8$).

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[1] The term "kayser" is used in this paper as a unit of wave number (formerly cm.$^{-1}$) as recommended by the Joint Commission for Spectroscopy, *J. Optical Soc. Am.*, **43**, 410 (1953).

[2] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 881 (1951).

[3] A. W. Weitkamp, THIS JOURNAL, **67**, 447 (1945).

[4] D. H. S. Horn, F. W. Hougen and E. von Rudloff, *Chemistry and Industry*, 106 (1953).

[5] J. Tiedt and E. V. Truter, *ibid.*, 403 (1952).

[6] D. H. S. Horn, F. W. Hougen, E. von Rudloff and D. A. Sutton, *J. Chem. Soc.*, 177 (1954).

[7] C. S. Barnes, R. G. Curtis and H. H. Hatt, *Australian J. Appl. Sci.*, **3**, 88 (1952).

The Disproportionation of Allylic Chlorofluoro Compounds[1]

BY MAURICE PROBER

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The utility of metal halides for the disproportionation of chlorofluoro compounds became of interest when an appreciable yield of a trichlorotrifluoropropene was isolated from a sample of tetrachloro-3,3-difluoropropene which had been contaminated with metal halides. Previously, aluminum halides have been used as disproportionation catalysts–aluminum chloride and bromide at moderate temperatures,[2] and aluminum fluoride at elevated temperatures.[3]

A series of metal halides was tested for catalytic activity by refluxing tetrachloro-3,3-difluoropropene with one mole per cent. of catalyst and noting qualitatively how fast the lower boiling trichlorotrifluoropropene was formed. The catalysts, arranged in order of decreasing activity, are antimony pentachloride > titanium tetrachloride > aluminum bromide, aluminum chloride > ferric chloride. Tin tetrachloride, zinc chloride, boron trifluoride etherate and aluminum fluoride did not effect disproportionation under these conditions.

The disproportionation of tetrachloro-3,3-difluoropropene by antimony pentachloride was repeated on a larger scale and the following reactions occurred

$$2CF_2ClCCl{=}CCl_2 \longrightarrow CF_3CCl{=}CCl_2 + CFCl_2CCl{=}CCl_2$$
$$2CFCl_2CCl{=}CCl_2 \longrightarrow CF_2ClCCl{=}CCl_2 + CCl_3CCl{=}CCl_2$$

Only the allylic chlorofluoro group was involved in the disproportionation. The identity of the products was proved by comparison of the physical constants with the literature values. In addition, the refractive indices of the isomeric chlorofluoro compounds which have been reported are different from those observed.

The yield data are summarized in Table I.

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[1] Presented at the 124th Meeting of the American Chemical Society, September, 1953.

[2] (a) U. S. Patent 1,994,035 (March 12, 1953); (b) U. S. Patent 2,426,637 (September 2, 1947); (c) U. S. Patent 2,426,638 (September 2, 1947); (d) W. T. Miller, E. W. Fager and P. Griswold, THIS JOURNAL, **72**, 705 (1950); (e) U. S. Patent 2,598,411 (May 27, 1952).

[3] U. S. Patent 2,478,201 (August 9, 1949); U. S. Patent 2,478,932 (August 16, 1949).

TABLE I

DISPROPORTIONATION OF TETRACHLORO-3,3-DIFLUOROPROPENE BY ANTIMONY PENTACHLORIDE

Time, hr.	Catalyst concn., mole %	Mole % $CF_3CCl=CCl_2$	Mole % $CF_2ClCCl=CCl_2$	Mole % $CFCl_2CCl=CCl_2$	Mole % $CCl_3CCl=CCl_2$
1	1	10	81	6	2
22	1	25	54	10	7
22	5	47	23	10	18

The equilibrium in this system is in the direction of the most highly fluorinated and least fluorinated compounds, $CF_3CCl=CCl_2$ and $CCl_3CCl=CCl_2$. A mixture of these two olefins is not disproportionated to the mixed chlorofluoro compounds by antimony pentachloride. In addition, the recovered tetrachlorodifluoropropene can be further disproportionated. The equilibrium position is in marked contrast to that in the carbon tetrachloride–carbon tetrabromide system, where the equilibrium favors the mixed product, dibromodichloromethane.[4] In the absence of a significant heat of reaction, the equilibrium is controlled by entropy effects, and the most random products are favored. However, the carbon–chlorine and carbon–fluorine bond energies change with an increasing number of fluorine atoms on the carbon atom.[5] This results in a significant heat of reaction which produces an equilibrium mixture which is quite different from that predicted by entropy considerations. This heat of reaction was observed in the disproportionation of dichlorofluoromethane to chloroform and fluoroform.[2c]

Disproportionation of another allylic compound, chlorodifluoromethylbenzene, proceeded rapidly with catalytic quantities of antimony pentachloride. A 76% yield of benzotrifluoride was obtained. However, most of the dichlorofluoromethylbenzene underwent a Friedel–Crafts polymerization with the elimination of hydrogen chloride.

Antimony pentachloride was ineffective in disproportionating saturated compounds, such as chlorotrifluoromethane and *sym*-tetrachlorodifluoroethane. These reactions were carried out under conditions where fluorination of these polychlorides by hydrogen fluoride occurs readily with a catalytic quantity of antimony pentachloride. This demonstrates that a rapid disproportionation reaction cannot be postulated to explain the catalytic role of pentavalent antimony in promoting the fluorination of saturated polychlorides.

Experimental

Disproportionation of Tetrachloro-3,3-difluoropropene with Antimony Pentachloride.—A solution of 225.5 g. (1.044 moles) of tetrachloro-3,3-difluoropropene and 15.6 g. (0.052 mole) of antimony pentachloride was refluxed for 22 hours. The reaction product was then stirred with dilute hydrochloric acid, washed with water, dried and rectified. There was obtained (a) 94.1 g. of 1,1,2-trichlorotrifluoropropene, b.p. 87.2–88.4°; (b) 6.0 g., b.p. 88.4–127.4°; (c) 64.6 g. of tetrachloro-3,3-difluoropropene, b.p. 64.6–65.1° at 90 mm.; (d) 3.4 g., b.p. 65.1° at 90 mm. to −75.6° at 33 mm.; (e) 20.0 g. of pentachloro-3-fluoropropene, b.p. 75.6–76.9° at 33 mm.; (f) 3.5 g., b.p. 76.9° at 33 mm. to 90° at 16 mm.; (g) 40.1 g. of hexachloropropene, b.p. 93.0–93.4° at 16 mm.; (h) 4.0 g. of residue.

The other experiments of Table I were carried out in a similar manner. In calculating yields, the intermediate fractions were divided equally into the two components.

Catalyst Evaluation with Tetrachloro-3,3-difluoropropene.—Approximately 0.2 mole of tetrachloro-3,3-difluoropropene and 1 mole % of catalyst were refluxed under a 10-plate glass helix-packed column. Since the disproportionation product 1,1,2-trichlorotrifluoropropene boils at 88°, the drop in reflux temperature was taken as a measure of catalyst activity in promoting disproportionation. The results are given below. In those cases where no drop in boiling point was observed, the refractive index checked that of the starting propene.

Catalyst	Observation
None	No change in 40 hours
Antimony pentachloride	Began refluxing at 87.8°
Aluminum bromide	89° after 4 hours
Aluminum chloride	92.5° after 4.5 hours
Ferric chloride	118° after 8 hours
Zinc chloride	No change in 24 hours
Stannic chloride	No change in 24 hours
Boron trifluoride diethyl etherate	No change in 24 hours
Aluminum fluoride	No change in 24 hours
Titanium tetrachloride	88.4° after 2 hours

Comparison of Physical Constants.—The appropriate fractions of the larger scale runs were combined and rectified, and the physical constants determined on large middle fractions.

	B.p., °C.	$n^{20}D$	d^{20}_4	F.p., °C.
$CF_3CCl=CCl_2$, Obsd.	88.1	1.4096	1.617	−114.6 to −114.2
Lit.[6]	88.3	1.4095	1.6188	−114.7
$CF_2ClCCl=CCl_2$, Obsd.	128.3	1.4575	1.659	−102.2 to −102.8
Lit.[6]	128.0	1.4573	1.6598	−103.0
$CFCl_2CCl=CCl_2$, Obsd.	170.1	1.5052	1.702	
Lit.[6]	170.2	1.5050	1.7041	Glass
$CCl_3CCl=CCl_2$, Obsd.	211.6	1.5491	1.766	
Lit.[7]	209–210	1.5091[8]	1.7652	

Attempted Disproportionation of 1,1,2-Trichlorotrifluoropropene and Hexachloropropene.—A solution of 99.8 g. (0.500 mole) of 1,1,2-trichlorotrifluoropropene, 119.5 g. (0.500 mole) of hexachloropropene and 14.9 g. (0.050 mole) of antimony pentachloride was refluxed for 22 hours, and worked up as above. Only starting materials were recovered. There was no evidence of distillation plateaus corresponding to difluorotetrachloropropene and fluoropentachloropropene in the 6.2-g. intermediate fraction.

Disproportionation of Chlorodifluoromethylbenzene.—A solution of 22.5 g. (0.075 mole) of antimony pentachloride (5 mole %) and 243.8 g. (1.50 moles) of chlorodifluoromethylbenzene was refluxed for one-half hour. Considerable hydrogen chloride was evolved. The reaction product was washed with dilute hydrochloric acid, water, and dried. The volatile products were removed up to b.p. 110° at 3 mm., leaving 70.4 g. of a black pitch-like residue. The distillate was rectified yielding (a) 110.5 g. of benzotrifluoride, b.p. 43.0–43.6° at 94 mm., 102.0–102.5° at 760 mm., $n^{20}D$ 1.4145; reported[9] b.p. 102.6°, $n^{25}D$ 1.4119. (b) 6.9 g., b.p. 43.6° at 94 mm. to 66° at 9.5 mm. (c) 7.6 g. of benzoyl chloride, b.p. 66–70° at 9 mm., 195–197° at 760 mm., $n^{20}D$ 1.5540; reported b.p. 73.0° at 10 mm., 197.2° at 760 mm.,[10] $n^{20}D$ 1.5537. (d) 9.7 g. of residue.

Disproportionation of Trichlorofluoromethane.—Trichlorofluoromethane, 25.0 g. (0.182 mole), and 2.7 g. (0.0091

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(4) G. S. Forbes and H. H. Anderson, THIS JOURNAL, **66**, 731 (1944).

(5) N. Muller, *ibid.*, **75**, 860 (1954); G. Glockler, "Fluorine Chemistry," Vol. I, J. H. Simons, Ed., Academic Press, Inc., New York, N. Y., 1950, pp. 347–354.

(6) A. L. Henne, A. M. Whaley and J. K. Stevenson, THIS JOURNAL, **63**, 3478 (1931).

(7) P. Fritsch, *Ann.*, **297**, 314 (1897).

(8) The literature refractive index is incorrect since it yields an erroneous molar refraction 42.09 (theory 44.75) and it is out of line with the extrapolated values from the chlorofluoropropene series. The observed refractive index yields a molar refraction of 44.89.

(9) P. E. Brown and T. De Vries, THIS JOURNAL, **73**, 1811 (1951).

(10) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

mole) of antimony pentachloride (5 mole %) were heated at 120° for 24 hours in a stainless steel bomb. The reaction product was rectified through a low temperature Podbielniak column yielding 0.84 g. (0.0069 mole) of dichlorodifluoromethane, 21.5 g. of trichlorofluoromethane and 1.2 g. (0.0078 mole) of carbon tetrachloride.

Disproportionation of *sym*-Tetrachlorodifluoroethane.—A solution of 5.7 g. (0.0191 mole) of antimony pentachloride in 77.5 g. (0.381 mole) of *sym*-tetrachlorodifluoroethane was refluxed as in the catalyst evaluation experiments. The boiling point at the still-head, 91.6°, was unchanged after 10 hours.

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The Separation of D-Glucose and D-Fructose from Invert Sugar or Sucrose[1]

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Cation exchange resins bearing the sulfonic acid group have been employed as catalysts for the condensation reactions of sugars with alcohols to give glycosides.[2,3] Resins of this type have also been used for the hydrolysis of disaccharides, starch and methylated polysaccharides.[3] The hydrolysis of sucrose by this means has been shown to proceed rapidly and quantitatively and the D-fructose may be isolated *via* calcium fructosate.[4]

Condensation reactions between compounds containing the carbonyl group and sugars or sugar derivatives such as glycosides and sugar alcohols have also been catalyzed by cation exchange resins.[2,3] In particular, D-fructose was found to give a high yield of 1,2-4,5-diisopropylidene-D-fructopyranose.[2] Under similar conditions D-glucose does not condense to any large extent with acetone.

A method using cation exchange resins is described herein for the separation of D-glucose from D-fructose. This has been achieved by using a combination of the aforementioned techniques. Thus, when a suspension of finely divided sucrose and a cation exchange resin in acetone containing a small amount (5%) of water is stirred at room temperature, simultaneous hydrolysis of the sucrose and condensation of the derived fructose with acetone take place with the formation of a clear solution. This stage is reached in about 18 hours and soon thereafter crystalline D-glucose begins to separate; eventually a nearly quantitative yield of D-glucose is produced. Invert sugar or a mixture of equal parts of D-glucose and D-fructose can also serve as starting materials. The supernatant solution contains principally the diisopropylidene derivative of fructose and following the removal of excess solvent this compound may be obtained in the crystalline form either directly from the sirup or after purification by solvent extraction. Crystalline D-fructose may then be regenerated by acid hydrolysis either from the crude sirupy diisopropylidene derivative or from the purified crystalline substance.

The success of the method outlined herein depends upon the presence of an empirically determined ratio of water to acetone in order to obtain crystalline D-glucose.

Experimental

Preparation of Resin.—The cation exchange resin, "Amberlite 1R-120,"[5] was regenerated in the usual manner with *N* hydrochloric acid, washed thoroughly with distilled water by decantation to remove all traces of mineral acid and finally washed several times with absolute alcohol and dried at room temperature *in vacuo*. No attempt was made to evaluate the effect of small amounts of mineral acid upon the reactions described herein.[3] In all cases recorded in this paper no mineral acid was detected in the reaction mixtures after removal of the resin.

Separation of D-Glucose from Invert Sugar.—A solution of sucrose (20 g.) in 0.1 *N* sulfuric acid (100 ml.) was heated for 1 hour at 90° on a water-bath. The solution was neutralized while hot with barium carbonate, treated with a little charcoal to facilitate removal of barium sulfate and filtered. Distillation of the solvent *in vacuo* gave the invert sugar as a colorless sirup which was dissolved in water (20 ml.) and shaken at room temperature with acetone (400 ml.) in the presence of Amberlite 1R-120 cation exchange resin (20 g.). After 1 day D-glucose had commenced to separate and crystallization appeared to be complete after 4 days. After 7 days the glucose and resin were filtered off, washed with acetone and dried in air (yield 31.5 g., D-glucose plus resin or 11.4 g. of D-glucose). It is apparent that the yield of D-glucose is nearly quantitative.

Separation of D-Glucose from Sucrose.—Sucrose (50 g.) and Amberlite 1R-120 cation exchange resin (50 g.) were suspended in a mixture of acetone (1000 ml.) and water (60 ml.) and the mixture gently stirred at room temperature. The following changes in the appearance of the reaction mixture were noted: after 14 hours, all the crystalline sucrose had dissolved and the solution was clear; after 24 hours, crystalline-D-glucose appeared and after 72 hours, crystallization appeared to be complete. The reaction mixture was filtered and the D-glucose and resin washed thoroughly with acetone and dried at room temperature. The total weight of D-glucose and resin amounted to 75.6 g. corresponding to a weight of D-glucose of 25.6 g. Without recrystallization the D-glucose so obtained showed $[\alpha]^{22}\text{D}$ +44.1° equilibrium value in water (*c* 4.3) and m.p. 130–146°. After one recrystallization the D-glucose showed $[\alpha]^{22}\text{D}$ +51.3° equilibrium value in water (*c* 1.0) and m.p. 143–146.

Attempts to duplicate the experiments in the absence of resin met with no success. Invert sugar will not crystallize from aqueous acetone in the absence of the resin treatment nor will sucrose or invert sugar afford crystalline D-glucose when mineral acid is substituted for the resin.

Isolation of 1,2-4,5-Diisopropylidene-D-fructopyranose.—The sirupy solutions derived from the reactions outlined above yielded α-diisopropylidene-D-fructose directly; however, separation of the crystalline derivative from such a sirup is difficult and unnecessary for the regeneration of D-fructose. If the crystalline α-diisopropylidene-D-fructose is required it may be extracted from the sirupy product with benzene, m.p. and mixed m.p. 117–118° (after recrystallization from light petroleum ether).

Regeneration of D-Fructose.—The sirup (22.8 g.), derived from the acetone supernatant solution following the separation of D-glucose from 50 g. of sucrose or invert sugar as described above, was hydrolyzed directly with 0.01 *N* sulfuric acid (220 ml.) at 90°. The solution showed the following change in rotation during hydrolysis: −2.42°, initial value (1-dm. tube); −4.58°, 6 hours; −4.87°, 12 hours (constant value). The hydrolysate was neutralized by passing it over an anion exchange resin (Duolite A-4)[6] and concentrated *in vacuo* to a sirup. This sirup showed upon paper chromatographic examination the presence of a

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[1] Paper No. 3132, Scientific Journal Series, Minnesota Agricultural Experiment Station, University of Minnesota, St. Paul. This paper will form part of a thesis to be submitted by D. S. to the University of Minnesota in partial fulfillment of the requirements for the degree of Ph.D.

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