to demonstrate the reaction as the ethylenediamine destroys the reagent). The blue solution fades in about fifteen minutes, but may be stabilized by extraction with butyl alcohol. Another glyoxaline (4,5-diphenylglyoxaline) has also been observed to give a blue color with Gibbs' reagent.

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The Protolytic Activity of Hydrogen Chloride and of Hydrogen Bromide in Ethyl Ether

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Hantzsch and Weissberger[1a,b] found a remarkable difference in the reaction rate of diazoacetic ester with hydrogen chloride and hydrogen bromide in ethyl ether as a solvent. While 0.01 M hydrogen bromide and diazoacetic ester in ether react at a rate similar to that in tetrachloroethane, (2.2^2), a 0.01 M solution of hydrogen chloride and diazoacetic ester in ether reacts about 10^4 times slower (0.00016^2). The difference between the two hydrogen halides, which appears to diminish at higher concentrations, is regarded as characteristic for the ethereal solutions of the hydrogen halides and not as specific for their reaction with diazoacetic ester because dimethylaminoazobenzene in ether containing 0.02 mole per liter of hydrogen chloride is less red than a solution containing 0.007 mole per liter of hydrogen bromide.[1a]

In order to test further the difference between ethereal solutions of hydrogen chloride and hydrogen bromide, *l*-menthone was used as a reagent.[3] The optical inversion of this compound was measured as described previously.[4] The data are listed in the table, $k + k' = \frac{1}{t} \log^{10} \frac{\rho_\infty - \rho_0}{\rho_\infty - \rho_t}$, where ρ_0, ρ_∞ and ρ_t are the rotation angles at the time of the first reading, at equilibrium and at a time t after the first reading, respectively.[4a]

MENTHONE 0.5 MOLE/LITER IN ETHYL ETHER, 20.0 ±0.1°

Acid	Concn. in mole/liter	$k + k'$	$(k + k')$/Concn.
HCl	0.05	0.0019 min.$^{-1}$	0.038 liters mole^{-1} min.$^{-1}$
HBr	.0005	.07	140
	.001	.15	150
	.0025	.36	144

In the interval measured, the rate is proportional to the concentration of hydrogen bromide. By means of a linear extrapolation, one calculates for the inversion of 0.5 M menthone with 0.05 M hydrogen bromide in ether a rate $(k + k') = 7.2$, which is 3.8×10^3 times higher than that found with 0.05 M hydrogen chloride.[4d] This confirms that the effect of ether on hydrogen chloride is not specific for the diazo ester decomposition. The factor for the menthone inversion (3.8×10^3) is smaller than for the diazo ester decomposition (1.4×10^4), presumably because the acid is more dilute in the diazo ester decomposition and the effect of the ether increases with greater dilution.

The rate of the menthone inversion with hydrogen bromide in ether is, in the range of the experiments, proportional to the concentration of the acid, while the inversion rate with hydrogen chloride is proportional to the square of the acid concentration.[4d] The latter dependence agrees with the mechanism of the menthone inversion with trichloroacetic acid in benzene,[4a] *viz.*, a transition from *l*-menthone to *d*-iso-menthone and *vice versa* by interaction of a binary acid menthone complex with a further molecule of the acid.

In the *reaction with diazoacetic ester*, 0.1 M hydrogen bromide has about the same rate in ether (2.2^2) and in tetrachloroethane (2.5^2), and 0.01 molar hydrogen chloride in tetrachloroethane has roughly the same rate (1.6^2). The corresponding rates[2] for the 0.02 M hydrogen halides are 3.6, 6 and 3, respectively. With 0.02 and 0.01 M hydrogen chloride in toluene, the rates are 0.28 and 0.022, respectively, *i. e.*, the reactivity of the hydrogen chloride in toluene is lower than in tetrachloroethane and shows a greater drop with the dilution than in the latter solvent. A direct comparison between the rate of the *menthone inversion* with hydrogen bromide in ether and that with hydrogen chloride in benzene is not possible because of the different dependency of the rate on the acid concentration which was mentioned above. However, it is noteworthy that the rate of the menthone inversion with 0.0025 M hydrogen bromide in ether is 0.36, while the rate of the inversion with 0.0048 M hydrogen chloride in benzene is 0.00067. An effect of the excess menthone on the hydrogen chloride may be responsible for the difference between the two hydrogen halides. However, the relatively low rate of both the menthone inversion and the diazo ester decomposition seems to indicate that there is also an interference of the aromatic solvent with hydrogen chloride.

This brings to mind that Kablukoff[5] obtained a crystalline compound from solutions of hydrogen chloride in benzene. The same author found a sinking of the molecular conductivity of hydrogen chloride in ether with increasing dilution. This observation was confirmed by Mounajed[6] and may indicate a peculiarity of solutions of hydrogen chloride in ether which has to do with their low protolytic activity.

No special experiments were made in order to make sure that the difference in the activity of

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(1) (a) Hantzsch and Weissberger, *Z. physik. Chem.*, **125**, 251 (1927); (b) Weissberger, Dissertation, Leipzig, 1924.

(2) Rate constant of 2nd order reaction at 0° in liters mole^{-1} min.$^{-1}$ (natural logarithms).

(3) A. Dörken, Dissertation, Leipzig, 1934.

(4) (a) Weissberger, THIS JOURNAL, **65**, 102 (1943); (b) **65**, 242 (1943); (c) **65**, 245 (1943); (d) Weissberger and Thomas, *ibid.*, **65**, 402 (1943).

(5) Kablukoff, *Z. physik. Chem.*, **4**, 429 (1889).

(6) Mounajed, *Comp. rend.*, **197**, **44** (1933).

hydrogen bromide and hydrogen chloride in ether is not caused by a reaction of hydrogen bromide with the solvent, forming ethanol and ethyl bromide. Such a reaction should be more rapid with hydrogen bromide, but it is not thought to be a probable cause of the difference. The observations of Hantzsch and Weissberger[1a] and of Dörken[2] call for a more thorough investigation and for comparative measurements of the conductivity of the two hydrogen halides in ether. None of this work is planned by the author. The above scant data and discussion may serve to draw attention to a rather interesting problem of acid catalysis.

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Acetates, Propionates and Butyrates of Simple Saccharides

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The lower saturated fatty acid esters of carbohydrates are usually prepared by acylation with a mixture of pyridine and the anhydride of the acid. After reaction is complete, the mixture is customarily poured onto ice and the ester is separated either by filtration or by solvent extraction of the aqueous medium. An alternative isolation procedure, which has apparently been used very little, involves separation of the ester by vacuum distillation of excess reactants and volatile products after esterification. This method has been applied to the preparation of starch esters by Mullen and Pacsu[1] and of pentapropionylglucose and pentabutyrylglucose by Hess and Messmer.[2]

The general applicability of this latter procedure is shown by the results presented here. It has been found that the sugar esters can be obtained in quantitative yield by concentration of the reaction mixture *in vacuo* after the esterification process is complete. The excess pyridine, anhydride and fatty acid formed, are removed,[3] leaving the ester in a good state of purity. Further appropriate purification procedures can then be applied if desired, depending on the properties of and intended uses for the particular ester. This method of operation has the following advantages: (1) ease of operation with a minimum of manipulative steps, and (2) increased yields of esters in many cases. It is particularly useful as compared to the conventional procedure when the desired ester is moderately water soluble (*e.g.*, levoglucosan triacetate).

By use of the procedure described, the acetates, propionates and butyrates of sucrose, diacetone D-glucose α-methyl-D-glucoside, D-sorbitol, levoglucosan and D-glucose have been prepared. Properties of the products are listed in Table I.

TABLE I

PROPERTIES OF THE SUGAR ESTERS[a]

Substance	Color	State	M. p., °C.	Rotation measurements $[\alpha]^{25}D$ in $CHCl_3$	Concn.	% Acyl Calcd.	% Acyl Found[f]
Sucrose octaacetate crude[b]	White	Crystals	84–86	+ 60.6	3	50.7	50.8
Sucrose octapropionate crude	White	Crystals	44–46	+ 52.7	1	57.7	57.7
Sucrose octabutyrate[c] crude	Brown	Sirup	....	+ 46.5	3	63.0	63.0
Diacetone D-glucose monoacetate crude	Off white	Crystals	51–58	− 34.3	2	14.2	15.6
Diacetone D-glucose monoacetate recryst.	White	Crystals	57–61.5	− 36.9	1	14.2	14.6
Diacetone D-glucose monopropionate[c] crude	Yellow	Sirup	....	− 32.2	2	18.0	19.7
Diacetone D-glucose monopropionate[c] distil.	Water-white	Sirup	120.5–123[d]	− 35.1	1	18.0	18.4
Diacetone D-glucose monobutyrate[c] crude	Yellow	Sirup	....	− 31.3	2	21.5	23.5
Diacetone D-glucose monobutyrate[c] distil.	Water-white	Sirup	121[d]	− 33.3	1	21.5	21.9
α-Methyl-D-glucoside tetraacetate crude	White	Crystals	98–102	+130.4	3	47.5	47.3
α-Methyl-D-glucoside tetrapropionate[c] crude	Viscous	Sirup	....	+114.5	3	54.5	54.8
α-Methyl-D-glucoside tetrabutyrate[c] crude	Brown fluid	Sirup	....	+102.6	2	59.9	60.1
D-Sorbitol hexaacetate crude	Slightly yellow	Crystals	91–97	+ 12.3	3	59.4	58.8
D-Sorbitol hexaacetate recryst.	White	Crystals	97–98.5	+ 10.6	3	59.4	59.2
D-Sorbitol hexapropionate[c] crude	Slightly yellow	Sirup	....	+ 14.1	4	66.0	65.6
D-Sorbitol hexabutyrate[c] crude	Brown	Sirup	....	+ 17.4	3	70.8	70.2
Levoglucosan triacetate crude	White	Crystals	107–110	− 61.5	1	44.8	44.2
Levoglucosan tripropionate[c] distil.	White	Crystals	37–38	− 56.8	2	51.8	52.0
Levoglucosan tributyrate[c] distil.	Colorless	Sirup	170[d]	− 34.5[e]	2	57.2	57.3
Pentaacetyl-D-glucose crude	White	Crystals	93–100	+ 73.2	1	55.1	54.9
Pentapropionyl-D-glucose crude	V. visc. lgt. yellow	Sirup	....	+ 53.7	2	62.0	61.6
Pentabutyryl-D-glucose crude	Visc. lgt. brown	Sirup	....	+ 44.5	2	67.0	67.0

[a] Melting points and boiling points are uncorrected. [b] The word "crude" is used in this table to indicate the whole of the ester fraction obtained as a residue upon distillation of the non-ester bodies. [c] These compounds are believed to be previously unreported in the literature. [d] Boiling point at <1 mm. pressure. [e] In methyl alcohol. [f] Average of duplicate determinations.

In the case of D-glucose a mixture of isomeric penta-esters was formed on acylation. A single product results whenever the hemiacetal hydroxyl group on carbon one is combined, so that change of configuration cannot occur.

Experimental

The general procedure used in preparing the esters was as follows: One-tenth mole of the sugar was mixed at room temperature with one and a half times the quantity of anhydride and two times the amount of dry pyridine

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(1) Mullen and Pacsu, *Ind. Eng. Chem.*, **34**, 1209 (1942).

(2) Hess and Messmer, *Ber.*, **54**, 499 (1921).

(3) Gardner, *ibid.*, **23**, 1567 (1890).