pounds. According to this view, the horizontal parts of the curves indicate that the residual fields present in the cellulose are temporarily neutralized by the formation of the compounds $(C_6H_{10}O_5)_{12}\cdot NaOH$ from native cotton and $(C_6H_{10}O_5)_{12}\cdot 2NaOH$ from mercerized cotton.

Summary

1. The absorption of sodium hydroxide by cotton has been shown to take place very rapidly, and to change only slightly over a period of two or three days.
2. Previous treatment of the cotton by sodium hydroxide solution of concentration greater than 5% increases its power of absorption. The maximum effect is produced when the concentration of the modifying solution is 20% or greater.
3. The absorption curves indicate that the action of sodium hydroxide solution of concentration 4 to 5% is the formation of the compounds $(C_6H_{10}O_5)_{12}\cdot NaOH$ from native cotton and $(C_6H_{10}O_5)_{12}\cdot 2NaOH$ from mercerized cotton.

GRAND FALLS, NEWFOUNDLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME]

A NEW METHOD OF PREPARING ACETALS

BY J. A. NIEUWLAND, R. R. VOGT AND W. L. FOOHEY

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Boron and silicon fluorides react readily with methyl or ethyl alcohols, forming heavy, fuming, almost colorless, and strongly acid liquids. These solutions have been studied by Liebig and Wöhler,[1] W. Knop,[2] Gay-Lussac and Thénard,[3] Kuhlman,[4] and V. Gasselin.[5] Due, however, to the complexity of the mixtures and to the instability of the compounds when isolated, the acids present have never been definitely identified. By distilling a solution of one mole of boron fluoride in one mole of methyl alcohol, Gasselin obtained an acid residue and the neutral compounds CH_3OBF_2 and $(CH_3O)_2BF$; but these in turn are decomposed by more alcohol with the liberation of acid. In the case of boron fluoride, the acid is probably HBF_4, or possibly H_3BF_6 or an ester acid, dissolved and ionized in absolute alcohol or some other constituent of the mixture. Orthoboric ester, which may be present, was shown by Walden[6] to be a

[1] Liebig and Wöhler, *Pogg. Ann.*, **24,** 171 (1832).

[2] W. Knop, *J. prakt. Chem.*, [1] **74,** 41 (1858).

[3] Gay-Lussac and Thénard, "Recherches physico-chimiques," Vol. II, p. 39.

[4] Kuhlman, *Ann.*, **33,** 205 (1840).

[5] V. Gasselin, *Ann. chim. phys.*, [7] **3,** 5–83 (1894).

[6] Walden, *Z. physik. Chem.*, **54,** 175 (1906).

good ionizing solvent; or CH_3OBF_2 and $(CH_3O)_2BF$ which are the fluorine derivatives of the ester may act in this way. Silicon fluoride apparently produces similar solutions of H_2SiF_6. Gases having the properties of diborane and silicane are formed on treating these solutions with a metal such as iron, zinc, magnesium or aluminum.

We have found these acids, especially the boron fluoride solution in methyl alcohol, to be much superior to sulfuric or any other acid in making ethylidene compounds from acetylene with mercuric oxide as catalyst. They did not attack glass, dissolved mercuric oxide readily, were lasting and effective in very low concentration, prolonged the usefulness of the mercury and formed only traces of tarry by-products. They did not remove halogens, ether or ester groups from compounds treated, and were easily separated from the finished product. By their use we have been able to prepare a number of new ethylidene ethers or acetals which could not be obtained from acetylene in the presence of sulfuric acid or by any other known process. These acids in the presence of mercuric oxide caused acetylene to combine with strong organic acids, alcohols, glycols, hydroxy acids, β-diketones and phenols, etc. The silicon fluoride solution especially, formed compounds with phenols, differing markedly from those produced in sulfuric acid. In reactions of acetylene with aryl hydrocarbons and phenolic ethers, these acids did not seem to be effective.

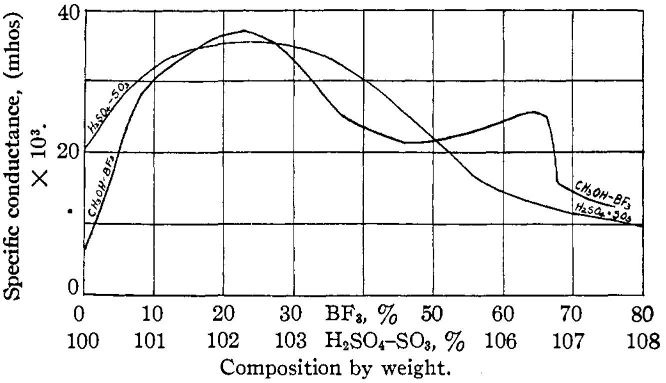


Fig. 1.—Specific conductance of the systems CH_3OH-BF_3 and $H_2SO_4-SO_3$.

Although boron or silicon fluorides passed directly into many organic hydroxyl compounds formed acid solutions and acted with mercuric oxide as catalysts for acetylene, it was found more convenient to make up a stock solution in methyl alcohol. A 55–73% solution of boron fluoride was generally used. The graph of the specific conductance of such a solution as compared with sulfuric acid indicated that it contained a strong non-aqueous acid (Fig. 1). The compound $BF_3 \cdot (C_2H_5)_2O$ (b. p. 124°)

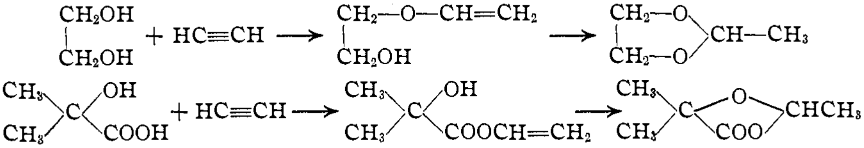
prepared from boron fluoride and ether could also serve as a catalyst, in which case the ether was liberated by the reacting compounds, and should be swept from the system by a stream of acetylene as free ether; when present in quantity it retarded catalysis in the alcoholic solution. Methyl alcohol dissolved only 37 parts by weight of silicon fluoride.

The reactions for the union of boron trifluoride and alcohol may perhaps be written according to the following scheme. Fluo acids may be present as shown by the conductive curve and the quantities of boron trifluoride absorbed by the alcohol at the concentrations when the curve has two maxima.

$$
\begin{aligned}
&(4BF_3 + 3CH_3OH \longrightarrow (CH_3O)_3B + 3HBF_4)\\
&BF_3 + 2(CH_3O)_3B \longrightarrow 3(CH_3O)_2BF\\
&BF_3 + (CH_3O)_2BF \longrightarrow 2(CH_3O)BF_2\\
\text{also } &(2BF_3 + 3CH_3OH \longrightarrow H_3BF_6 + (CH_3O)_3B), \text{ etc.}
\end{aligned}
$$

I. Acetals of Glycols, Oxy-acids and Other Derivatives.—Several acetals have previously been prepared by the action of acetylene on alcohols in the presence of mercuric sulfate and sulfuric acid by Nieuwland and co-workers.[7] Hill and Hibbert[8] obtained a series of cyclic acetals from glycols by a somewhat similar method.

Using the alcoholic solutions of boron or silicon fluorides with mercuric oxide as catalysts, we have prepared from acetylene the acetals of polyhydric alcohols and of their ethers, chlorohydrins and of the hydroxy acids and their esters. All of these reactions are presumed to take place in two steps;[9] (a) addition of acetylene to form a vinyl ether, (b) spontaneous change of the vinyl ether to the acetal in acid solutions by rearrangement in the case of polyhydric alcohols or by addition of a second molecule in the case of monohydric compounds, according to the following scheme of reactions



The procedure is nearly uniform for all substances treated and may be illustrated by the case of ethylidene glycol.

Experimental

Five grams of a 55–65% solution of boron fluoride in methyl alcohol was weighed into a tared flask and one gram of mercuric oxide partly dissolved in it by gentle heating. The flask was then cooled, 102 g. of ethylene glycol added and the whole well mixed. Dry acetylene from a gasometer was then passed into the closed flask with occasional

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[7] Reichert, Bailey and Nieuwland, THIS JOURNAL, **45**, 1552 (1923).

[8] Hill and Hibbert, *ibid.*, **45**, 3108 (1923).

[9] *Cf.* Hill and Pidgeon, *ibid.*, **50**, 2718 (1928).

shaking until the calculated weight had been absorbed.[10] Potassium carbonate and a small quantity of water were then added to neutralize the acid and the acetal layer was separated, dried over potassium carbonate and fractionated.

Special adaptations of the procedure were made to fit certain cases. The quantity of acid required varied. A portion of glycerol acetal containing 0.142 g. of boron fluoride solution from a previous run was sufficient to catalyze 250 g. of glycerol to the acetal. One gram of mercuric oxide ordinarily would catalyze about 20 g. of acetylene to the ethylidene group, but to prevent too violent a reaction the oxide was ordinarily added in one to two-gram portions when it was needed, *e. g.*, as indicated by slow absorption of acetylene. A solvent, preferably ethylidene glycol, was used with some of the solids of higher melting point, such as dimethylcitric acid, benzilic acid and mandelic acid. The acetylene was catalyzed to the ethylidene group, simultaneously removing the hydrogen of the hydroxyl and carboxyl groups. The 1-hydroxy-carboxylic groups seemed to be more readily attached to form ethylidene groups than 2- or 3-hydroxy acids. Other lower melting solids such as pinacol and pentaerythritol were simply moistened with the acid mercury oxide catalytic solution and they slowly liquefied during acetal formation. In the case of viscous liquids or solids, care must be taken to avoid local overheating by cooling the reaction flask. The speed of acetylene absorption often increased as more acetal was formed due to the greater solubility of the acetylene in it. This was especially noticeable with glycerol. The reaction might be speeded by adding a portion of glycerol acetal from a previous run at the very start. When the hydroxyl groups or hydroxyl and carboxylic groups in a compound were present in even number, the absorption of acetylene stopped quantitatively when all their labile hydrogens were replaced with ethylidene group. In other cases an excess of acetylene which might combine to form more complex compounds must be avoided. Glycerol, for example, formed first ethylidene glycerol. This acetal, either in the original mixture or after separation, formed *ter*-ethylidene-*bis*-glycerol when treated with additional acetylene in the presence of the catalyst. In separating the high-boiling acetals ether was first added, then potassium carbonate and then water. The acetal ether layer was separated and dried over anhydrous potassium carbonate, and the liquids fractionated or crystallized in an appropriate solvent, preferably alcohol.

Where available, purified commercial preparations were treated to form acetals but the following substances were prepared in this laboratory: (1) hydroxyisobutyric acid was made by saponifying the commercial ethyl ester with sodium hydroxide, precipitating the zinc salt, treating with hydrogen sulfide and removing the water by vacuum distillation at 45°. The acid sublimed at 50°. (2) β-Methyl malate[11] was made by refluxing 120 g. of malic acid with methyl alcohol in a tared flask and then removing the water and alcohol by vacuum distillation. This process was repeated until the weight of the non-volatile residue had increased by 12 g. (3) Dimethyl citrate (symmetrical) was prepared by the method of Schroeter and Schmitz.[12]

Table I shows the ethylidene compounds prepared by this new method, their physical constants and the yields obtained.

In explanation of this table it might be said that the compounds here listed were all purified by redistillation when possible. The products from pentaerythritol and benzilic acid were recrystallized from ethyl alcohol and that from dimethyl citrate from methyl alcohol since ethyl alcohol seemed to cause partial displacement of the methyl groups by

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[10] *Cf.* "Organic Syntheses," Vol. IV, John Wiley and Sons, Inc., New York, **1925**, p. 28.

[11] *Cf.* Desmondesir, *Compt. rend.*, **33**, 229 (1851).

[12] Schroeter and Schmitz, *Ber.*, **35**, 2086 (1902).

ethyl. The ethylidene glycerol described was largely the 1,2-compound separated from its isomer by fractional distillation. Benzoylation of the original mixture of ethylidene glycerols by the method of Hill and Hibbert[13] showed that it consisted of 78% of 1,2-acetal and 22% 1,3-acetal. The ethylidene methyl ethyl pinacol was a mixture of isomers that could not be separated by fractionation, probably because of the presence of several racemic and meso isomers.

TABLE I

PREPARATIVE DATA AND PHYSICAL CONSTANTS OF COMPOUNDS

Asterisks denote new compounds.

	Taken,	Yield,				
Ethylidene compound	g.	g.	%	B. p., °C.	d_4	n_D
Ethylene glycol	102	88	62	82.3	0.9770^{24}	1.3945^{24}
Trimethylene glycol	93	55	45	108–111	0.9675^{23}	1.4160^{23}
Pinacol	...	...	...	133–134	....	......
Methylethyl pinacol*	...	...	...	150–180	....	......
Glycol methyl ether	150	77	44	87–91 (15 mm.)	0.9691^{25}	$1{,}4181^{25}$
Glycol ethyl ether	300	255	74	110–114 (14 mm.)	0.9328^{25}	1.4163^{25}
Glycol butyl ether*	200	115	52	142–146 (14 mm.)	0.9072^{26}	1.4263^{26}
Diethylene glycol*	...	...	...	250 (14 mm.)	....	......
Diethylene glycol ethyl ether*	...	...	...	140–145 (14 mm.)	....	......
Glycerol	...	...	(65–75)	189–191	1.1193^{24}	1.4395^{24}
Ter-ethylidene-*bis*-glycerol	542	322	41.7	160–162 (14 mm.)	1.1067^{24}	1.4482^{20}
Glycerol methyl ether*	141	105	60	145–147	1.0098^{24}	1.4145^{24}
Glycerol ethyl ether*	...	...	...	170–171	....	......
Glycerol phenyl ether*	150	119	68	142–144 (14 mm.)	(m. p. 29°)	
Bis-ethylidene-pentaerythritol*	69	86	90	113 (14 mm.)	(m. p. 40°)	
Ter-ethylidene-mannite	100	67	47	165–168 (17 mm.), sublimed at 90°		
Ethylene chlorohydrin	304	250	71	106–107 (14 mm.)	....	......
Trimethylene chlorohydrin*	157	70	38	127–129 (14 mm.)	....	......
Glycerol chlorohydrin	611	543	72	147–149	1.1720^{24}	1.4410^{24}
Glycerol monoacetin*	260	153	49	91.5–92 (14 mm.) 200–201 (760 mm.)	1.1110^{26}	1.4323^{26}
Lactic acid	240	179	61	149–151	1.074^{26}	1.4120^{26}
1-Hydroxy-isobutyric acid*	148	125	71	150 ± 0.3 (745 mm.)	1.0226^{28}	1.4034^{28}
Bis-ethylidene tartrate	...	...	...	122–128 (17 mm.)	....	......
Dimethyl tartrate*	184	172	81	137 ± 0.2 (16 mm.)	1.2306^{27}	1.4426^{27}
Diethyl tartrate*	162	137	74	147 ± 0.5 (18 mm.)	1.1408^{25}	1.1438^{25}
Methyl malate*	120	40	26	121–122 (15 mm.)	1.1975^{26}	1.4397^{26}
Ethyl malate*	118	50	30	125–130 (17 mm.)	1.1215^{26}	1.4402^{26}
Dimethyl citrate*	93	30	31	(m. p. 73°)		
Mandelic acid*	82	62	64	142–144 (14 mm.)	1.1681^{25}	1.4145^{25}
Benzilic acid*	86	64	66	198–200 (17 mm.) (m. p. 77°)		

The alkyl ester radicals could be removed from dimethyl and diethyl ethylidene tartrate by incomplete saponification, leaving ethylidene tartaric acid in solution, and extraction with ether of the excess of acetal ester. The following salts were prepared from this solution: sodium and calcium, as non-crystallizing sirups; zinc, crystalline, insoluble in water; cobalt, cadmium, copper, manganese and ammonium, soluble and crystalline; mercurous and stannic somewhat insoluble gels. The ammonium salt was the most stable. The others decomposed slowly when moist into acetaldehyde and the corresponding tartrates.

The degree of purity of some of these ethylidene compounds may be

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[13] Hill and Hibbert, THIS JOURNAL, **50, 2247** (1928); *cf.* J. P. Van Roon, *Rec. trav. chim.*, **48,** 173–190 (1929).

judged by comparing the analysis in Table II with the composition calculated from the formula.

TABLE II

ANALYTICAL DATA

Ethylidene compound	Wt. taken, g.	CO_2, g.	H_2O, g.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Glycerol α-phenyl ether	0.1704	0.4206	0.1093	68.0	67.3	7.22	7.17
Glycerol monoacetin	.1610	.3109	.1065	52.5	52.7	7.50	7.40
1-Hydroxyisobutyrate	.2705	.5504	.1855	55.4	55.5	7.69	7.65
Dimethyl tartrate	.2417	.4154	.1201	47.1	46.9	5.88	5.66
Diethyl tartrate	.2675	.4971	.1657	51.7	50.8	6.90	6.93
β-Methyl malate	.1804	.3244	.0987	48.3	48.2	5.75	6.00
Dimethyl citrate	.1775	.3193	.0899	48.8	49.0	5.69	5.67
Mandelate	.1848	.4604	.0941	67.4	67.9	5.62	5.70
Benzilate	.2374	.6610	.1184	75.6	75.9	5.51	5.57

The following substances reacted with acetylene to form derivatives, presumably acetals, but special difficulties accompanied the separation or purification.

The product from 1,2-diphenylglycol gave a solid product, m. p. 107–115°, b. p. 203–206°, but attempts to crystallize it from alcohol tended to remove the ethylidene group, leaving the crystals of the glycol. Diethyleneglycol ethyl ether (carbitol) reacted very energetically and smoothly, forming a liquid acetal that could not be distilled in a vacuum in larger quantities without decomposition; since it contained glycol, this could be removed as the low-boiling acetal. A method of determining the glycol in carbitol might be used to obtain the percentage of glycol quantitatively. Glycerol dichlorohydrin formed a high-boiling liquid product. Glycerol bromohydrin would not react at all. Bromine was apparently removed, which prevented catalysis. Trimethyleneglycol acetal in very pure condition (b. p. 110°) is obtained by this method in good yield.

p-Chlorophenyl-α-ether of glycerol, b. p. 173–175° at 17 mm., and also the *o*-chloro ether could not be crystallized. *o*-Cresyl glycerol ether (b. p. 165–167° at 17 mm.) and also the *p*-cresyl ether were non-crystallizable liquids.

Diethyl racemate reacted as readily as the tartrate. The physical constants approached those of the tartrate. Diethyl mesotartrate (b. p. 135–138° at 17 mm., n_D 1.4433) is a liquid.

2,2,2-Hydroxydiphenylpropionic acid (b. p. 181–183° at 10 mm.) reacted smoothly but the isolation of the compound could not be uniformly repeated. Diethyl citrate also reacted with acetylene but the product could not be isolated. Glucose cyclo-acetoacetic ester[14] formed a solid compound, boiling at 195° at 5–6 mm., but rapidly decomposed during crystallization.

It is peculiar that glycolic acid does not react and that its presence prevents the reaction of other compounds that do form acetals in its absence. It seemed to have as marked an anticatalytic effect as that of the presence of halogen ions. Quite a number of other glycols and hydroxy acids, as well as derivatives of these, gave smooth reactions with acetylene, but the compounds were not isolated since special difficulties were encountered in their purification. We may conclude, however, that this method of making acetals may be considered to be quite general and practical in application.

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[14] E. S. West, *J. Biol. Chem.*, **74**, 562 (1927).

Summary

1. Boron or silicon fluoride dissolved in an alcohol forms with mercuric oxide a catalyst for acetylene reactions much superior to sulfuric acid.
2. Fluoboric and fluosilicic acids are probably the active constituents of these solutions, which have high electrical conductance and strong acid properties (Fig. 1).
3. Boron fluoride dissolved in ether to form $BF^3(C_2H_5)_2O$, b. p. 123° may also be used as a catalytic agent.
4. The catalysts are effective in very small quantities.
5. Using these catalysts, ethylidene ethers have been prepared from glycols, hydroxy acids and their derivatives by the acetylene method.
6. A number of these compounds have not previously been prepared and could not be made by any known methods from acetylene or from acetaldehyde.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A STUDY OF THE DEHYDRATION OF DERIVATIVES OF ORTHO-BENZOYLBENZOIC ACID

BY GREGG DOUGHERTY AND A. H. GLEASON

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In a previous paper[1] it was stated that various methods for dehydrating *o*-benzoylbenzoic acid had been tried and that concentrated sulfuric acid appeared to be almost a specific for the conversion of this acid to anthraquinone. Velocity measurements gave a good constant at a variety of temperatures when values were substituted in the equation for a monomolecular reaction and the constancy was unaffected when the ratio of molecular concentrations was reduced to 13:1 (6:1 by weight), the lowest practical ratio.

The purpose of this work has been to compare the ease of formation of substituted anthraquinones from the corresponding substituted *o*-benzoylbenzoic acids. The method of carrying out the condensation was exactly the same as in the case of the unsubstituted acid, namely, equimolecular amounts of the reactants were dissolved in equal weights of concentrated sulfuric acid and the solutions were heated in a constant-temperature bath for a definite length of time.

Although a great variety of substituted *o*-benzoylbenzoic acids may be made by the Friedel-Crafts reaction, it was found that by no means all of them could be made to yield the corresponding anthraquinone, at least by the method which we used. In some cases traces of the anthraquinones were found but the yields were so small and the reaction product so com-

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[1] Dougherty and Gleason, THIS JOURNAL, **51**, 310 (1929).