It was hoped that this method of alkylation could be applied to the thiophenols, but S-alkylation occurred instead of C-alkylation to give good yields of the ethylsulfides. Table II summarizes the results obtained with thiophenols.

TABLE II[a]

ALKYLATION OF THIOPHENOLS WITH ETHANOL

	Moles thio-phenol	Moles ethanol	Temp., °C.	S. V.[b]	% Conversion to ethylaryl-sulfide[c]
Thiophenol	0.5	0.5	450	708	13.3[d]
Thiophenol	1.0	1.0	350	639	62.0
p-Methylthiophenol	0.24	0.24	350	633	55.0[d]
p-Methylthiophenol	0.75	1.12	350	515	74.0

[a,b] See Table I. [c] In every case most of the unreacted thiophenol was recovered producing yields of nearly 90%. Still better conversions could be obtained by using larger ratios of alcohol to thiophenol since there was almost no tendency to form higher alkylated products. (Traces of C-alkylated thiophenols were obtained.) [d] The ethylarylsulfides were identified by means of their boiling points as follows: ethylphenyl sulfide (Stadler, *Ber.*, **17**, 2077 (1884)), b. p. 202.5° (730 mm.) and *p*-methylphenyl sulfide (Otto, *Ber.*, **13**, 1277 (1880)), 222–223°. The structure of the two sulfides was also confirmed by comparison with a sample of each made from the thiophenol and from diethyl sulfate. Ethylphenylsulfide both catalytic and from diethyl sulfate had the same refractive index n^{25}_{D} 1.5640, as did *p*-methylphenyl sulfide n^{25}_{D} 1.5544.

As with the phenols the straight alumina catalyst was found to be just as effective as thoria on alumina. The catalyst activity did not appear to decrease appreciably during runs of a few hours duration. No darkening of the catalyst occurred. Actually it appeared to be somewhat bleached by use. The condensation products were almost water white. Higher temperatures did not result in appreciable amounts of C-alkylation.

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RECEIVED JANUARY 31, 1950

Benzylidene Derivatives of L-Arabinose Diethyl Acetal and Dimethyl Acetal[1]

BY CHARLES F. HUEBNER,[2] RUSSELL A. PANKRATZ AND KARL PAUL LINK

L-Arabinose diethyl mercaptal condenses rapidly with benzaldehyde in the presence of hydrogen chloride to yield a dibenzylidene compound (I) which must be removed immediately after the completion of the reaction because it is further transformed in this environment to sirupy decomposition products. The following evidence shows I to be 2,3;4,5-dibenzylidene-L-arabinose diethyl mercaptal. By mild acetic acid hydrolysis it was possible to obtain a monobenzylidene derivative (II) which consumes one molar equivalent of lead tetraacetate to produce formaldehyde. This behavior eliminates five of the possible six isomeric monobenzylidene mercaptals and shows II to be 2,3-benzylidene-L-arabinose diethyl mercaptal. Barring rearrangement during the hydrolysis of I to II the latter must have the proposed structure.

The divalent sulfur atoms in II complicate the oxidation since they appear also to consume tetraacetate. The oxidation of divalent sulfur by periodate has been indicated.[3] Controls run on I and on D-galactose diethyl mercaptal tetraacetate showed that one molar equivalent of oxidant was consumed within five to fifteen minutes and a second within two hours. This is presumably due to an almost immediate oxidation of the first sulfur followed by a much slower oxidation of the second. II, in contrast to these two compounds (Fig. 1), used up two molar equivalents within five minutes and four within two hours. The rapid consumption (within five minutes) of the extra molar equivalent of tetraacetate by II above the one molar equivalent used in the control oxidations of I and D-galactose diethyl mercaptal tetraacetate is accounted for by the presence of a glycol grouping in II. To detect the presence of formaldehyde among the primary oxidation products of II, the oxidation was carried out with only two molar equivalents of tetraacetate, thus preventing the formation of formaldehyde by a more extensive degradation involving hydrolysis and further oxidation by excess tetraacetate.

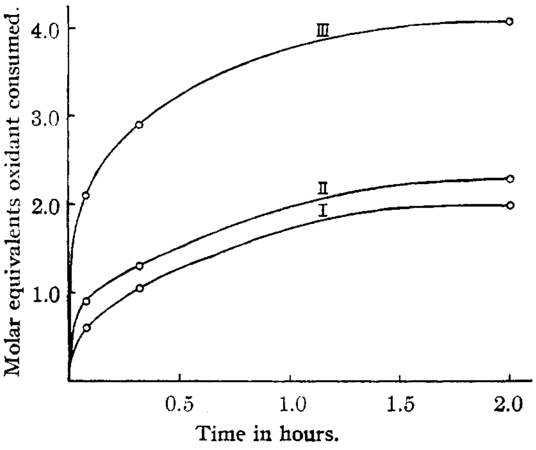

Fig. 1.—Oxidation of D-galactose diethylmercaptal tetraacetate (I), 2,3–4,5-dibenzylidine-L-arabinose mercaptal (II) and 2,3-benzylidene-L-arabinose diethylmercaptal (III) with lead tetraacetate (5.85 molar equivalents).

I was demercaptalated in methyl alcohol according to the general procedure of Green and Pacsu[4] yielding the dibenzylidene dimethyl acetal (III). III was subjected to hydrogenolysis over platinum and L-arabinose dimethyl acetal (IV)

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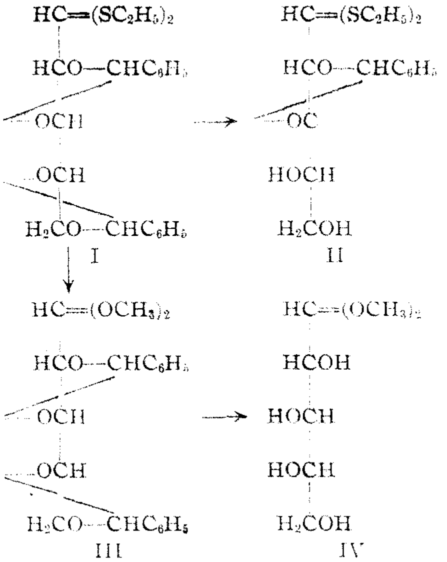
[1] Published with the approval of the Director of the Wisconsin Agricultural Experiment Station.

[2] Ciba Pharmaceutical Products, Inc., 556 Morris Avenue, Summit, N. J.

[3] Nicolet and Shinn, THIS JOURNAL, **61**, 1615 (1939).

[4] Green and Pacsu, *ibid.*, **59**, 1205 (1937).

resulted. The physical constants agree well with those of the enantiomorph prepared by another method as reported by Montgomery, *et al.*[5]



Experimental

2,3;4,5-Dibenzylidene-L-arabinose Diethyl Mercaptal (I).—Dry hydrogen chloride was bubbled through a suspension of 25 g. of L-arabinose diethyl mercaptal[6] in 40 ml. of benzaldehyde cooled to 0°. Solution which occurred after about five minutes was followed by crystallization of I. The crystals were immediately filtered, washed with Skellysolve B and after two recrystallizations from this solvent, 10 g. of long silky needles resulted; m. p. 103–105°, $[\alpha]^{25}\text{D}$ −12.2° (*c*, 5%; $CHCl_3$).

Anal. Calcd. for $C_{23}H_{28}O_4S_2$: C, 63.8; H, 6.5. Found: C, 63.7; H, 6.5.

2,3-Benzylidene-L-arabinose Diethyl Mercaptal (II).—Three grams of I was refluxed with 95 ml. of ethanol, 25 ml. of water and 75 ml. of glacial acetic acid for one hour. The solution was concentrated *in vacuo* to dryness and the residue recrystallized twice from a large volume of water, 1.8 g. of II resulting; m. p. 102–103°, $[\alpha]^{25}\text{D}$ −25° (*c*, 1.8; $CHCl_3$).

Anal. Calcd. for $C_{16}H_{24}O_4S_2$: C, 55.8; H, 7.0. Found: C, 55.9; H, 7.2.

Lead Tetraacetate on I, II and D-Galactose Diethyl Mercaptal Tetraacetate.—0.1 millimole of the test substance was weighed into a 10-ml. volumetric flask and made up to volume with 0.0585 *M* lead tetraacetate in acetic acid. Two-ml. aliquots were withdrawn for lead tetraacetate determinations.[7]

206 mg. of II was treated with two molar equivalents of 0.0585 *M* lead tetraacetate. After five minutes the mixture was poured into 100 ml. of water and neutralized with potassium hydroxide. An excess of dimedon reagent was added and after standing several hours, 90 mg. of the formaldehyde condensation product was collected, m. p. 187–189°. A melting point of the mixture with an authentic sample showed no depression. No formaldehyde could be detected when II or D-galactose diethyl mercaptal tetraacetate were treated with two molar equivalents of oxidant.

2,3;4,5-Dibenzylidene-L-arabinose Dimethyl Acetal (III).—To a mixture of 15 g. of II and 20 g. of yellow mercuric oxide in 300 ml. of methanol, was added dropwise over a period of one-half hour a solution of 20 g. of mercuric chloride in 200 ml. of methanol. After three hours under reflux, the mercury salts were filtered and 5 ml. of pyridine was added to the filtrate. After twelve hours at 3° a small amount of the pyridine–mercuric chloride complex was removed. The solution was concentrated *in vacuo* till crystals appeared, filtered and the operation repeated until no more crystalline material could be obtained. This material proved to be a mixture of the pyridine–mercuric chloride complex and III. A separation was made by virtue of the latter's solubility in hot Skellysolve B. It was recrystallized from this solvent; weight 6 g., m. p. 67–70°, $[\alpha]^{25}\text{D}$ +18.4° (*c*, 1; methanol).

Anal. Calcd. for $C_{21}H_{24}O_6$: C, 67.8; H, 6.5. Found: C, 67.7; H, 6.4.

The pyridine–mercuric chloride complex can be recrystallized from methanol, m. p. 196–197°.

Anal. Calcd. for $C_5H_5N\cdot HgCl_2$: C, 17.1; H, 1.4. Found: C, 17.0; H, 1.4.

L-Arabinose Dimethyl Acetal (IV).—300 mg. of III in 25 ml. of methanol was hydrogenated at one atmosphere over 20 mg. of platinum oxide. Twelve hours were required for the consumption of the requisite amount of hydrogen. After concentration *in vacuo* of the solution to a few ml., 100 mg. of V was obtained; m. p. 120–121°, $[\alpha]^{25}\text{D}$ +20.5° (*c*, 0.6; methanol). Montgomery, *et al.*,[5] report a m. p. of 122° and $[\alpha]\text{D}$ −18.5° (water) for the enantiomorph.

Anal. Calcd. for $C_5H_{10}O_4(OCH_3)_2$: OCH_3, 33.3. Found: OCH_3, 33.0.

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RECEIVED MAY 23, 1950

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[5] Montgomery, Hann and Hudson, THIS JOURNAL, **59**, 1124 (1937).

[6] Fischer, *Ber.*, **27**, 673 (1894).

[7] Hockett, Dienes and Ramsden, THIS JOURNAL, **65**, 1474 (1943).

Periodate Oxidation of D-Glucosazone

BY CHARLES F. HUEBNER[1] AND KARL PAUL LINK

During the course of some studies carried out several years ago involving the application of the periodate oxidation to certain amine and hydrazine derivatives in the carbohydrate class, the oxidation of D-glucosazone was studied. Since that time a paper has appeared on the latter subject.[2] We wish to record a few supplementary facts. A 60% dioxane–40% water mixture was found superior to ethanol because of its greater solvent power for both the osazone and the oxidant. Sodium periodate was used as the oxidant to allow for a determination of the acid produced during oxidation. Thus with D-glucosazone, two moles of formic acid (as shown by titration), one of formaldehyde (isolated as the formaldimedon compound) and one of the 1,2-bisphenylhydrazone of mesoxaldehyde (I) were produced in a rapid reaction with the consumption of three moles of the oxidant. To characterize I, the tris-phenylhydrazone (II) was compared with a sample prepared according to von Pechmann.[3]

An interesting transformation of II was observed. By recrystallization from acetic acid or ethanol containing mineral acid, after formation

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[1] Ciba Pharmaceutical Products, Inc., Summit, N. J.

[2] Chargaff and Magasanik, THIS JOURNAL, **69**, 1459 (1947).

[3] von Pechmann and Jenisch, *Ber.*, **24**, 3255 (1891).