

Oxythiamine picolonate, m. p. 130–133°. *Anal.* Calcd. for $C_{12}H_{15}O_2N_2S(C_{10}H_8O_2N_4)_2$: C, 48.36; H, 4.03. Found: C, 48.00; H, 4.15.

2-Methyl-4-oxypyrimidine-5-methylsulfonic Acid.—

Oxythiamine hydrochloride was treated with sulfite according to the method of Williams and co-workers.¹⁰ After standing with the sulfite for two days (faint Prebluda-McCollum reaction), the solution was adjusted to pH 10, the thiazole fragment removed by extraction with chloroform, and the oxysulfonic acid isolated according to the method used by Cline, *et al.*,¹³ in their synthesis of this compound.

Anal. Calcd. for $C_6H_8N_2SO_4$: C, 35.29; H, 3.92. Found: C, 35.70; H, 3.84.

The substance was also prepared as follows: The amino-sulfonic acid, obtained by treatment of thiamine with sulfite,¹⁰ was treated with the nitrogen oxide gases. The deamination could be easily followed, since the amino-sulfonic acid is insoluble, whereas the oxysulfonic acid is rather soluble. The solution was evaporated to dryness *in vacuo*, and recrystallized by solution in water and precipitation with alcohol.¹³

Anal. Found: C, 35.54; H, 4.03.

Bromoxythiamine Bromide Hydrobromide.—One gram of thiamine hydrochloride was dissolved in 20 ml. of glacial acetic acid saturated with dry hydrogen bromide, and sealed in a bomb tube. The mixture was heated at 150–160° for three hours. After removal from the tube, the solution was concentrated *in vacuo* to dryness. The residue was recrystallized several times by solution in methanol and precipitation with absolute ether.¹⁴ The resulting material was washed with ether and dried. It melted at 206–208° with decomposition. The compound does not form thiochrome and does not react with the Prebluda-McCollum reagent.

Anal. Calcd. for $C_{12}H_{16}N_2SOBr_3$: C, 29.38; H, 3.26; Br, 49.00. Found: C, 29.51; H, 3.87; Br, 49.05.

(13) Cline, Williams, Ruehle and Waterman, *THIS JOURNAL*, **59**, 530 (1937).

(14) Weil-Malherbe, *Biochem. J.*, **34**, 980 (1940).

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Dichlorovinyltrichlorosilanes

BY G. H. WAGNER AND A. N. PINES

In a recent publication,¹ Agre has described the preparation of " α,β -dichlorovinyltrichlorosilane." In the interest of clarifying the structure of his compound, we would like to record the properties and reactions of two dichlorovinyltrichlorosilanes prepared in this Laboratory. Our data indicate that his compound is β,β -dichlorovinyltrichlorosilane. The properties of our dichlorovinyltrichlorosilanes, I and II, are compared below with Agre's compound.

	Compound		Agre's compound
	I	II	
Boiling point { °C.	163.5–164	162.5–163	159
Mm.	750	750	729
Density, g./cc. at 25°C.	1.56	1.54
n_D^{20}	1.4958	1.4942	1.4942

Compound I on treatment with concentrated potassium hydroxide gave 1,2-dichloroethylene

(1) Agre, *THIS JOURNAL*, **71**, 300 (1949).

by fission of the carbon-silicon bond similar to that observed² for chloromethyl groups attached to silicon. An explosive gas, probably chloroacetylene, was also formed during this treatment. Compound II, which compares well in its properties with Agre's compound, gave 1,1-dichloroethylene on similar treatment with concentrated potassium hydroxide solution. These reactions indicate that compound I is α,β -dichlorovinyltrichlorosilane and compound II is β,β -dichlorovinyltrichlorosilane. Since the properties of these compounds are almost identical, within experimental error, the part of Agre's proof of structure which is based on a comparison of the physical properties of the compounds obtained from the reaction of trichlorosilane with trichloroethylene and with 1,2-dichloroacetylene is questionable.

Experimental

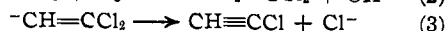
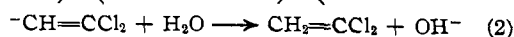
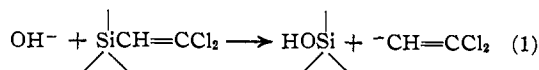
Treatment of Compound I with Concentrated Potassium Hydroxide.—A three-liter flask was fitted with a dropping funnel and a small water condenser. The water condenser was vented to the atmosphere through two traps, one cooled in ice-water and one in Dry Ice and acetone. A solution of 200 g. of potassium hydroxide in 1500 cc. of water was added to the flask. Seventy-seven grams of compound I was added rapidly through the dropping funnel to the potassium hydroxide solution. After heating the mixture for a few minutes at reflux, a water-insoluble liquid formed. This was steam distilled into the traps after shutting off the cooling water to the water condenser. Upon cooling, a violent explosion occurred in the vent lines but 6 g. of material with the following properties was recovered from the traps.

	Unknown	Reported for 1,2-dichloroethylene	
		<i>cis</i>	<i>trans</i>
Boiling point, °C.	56	48.4	60.3
Density { g./cc.	1.245	1.265	1.29
°C.	25	15	15
n_D^{20}	1.4501	1.4490, 15°	1.4519, 15°

Treatment of Compound II with Concentrated Potassium Hydroxide.—Using the same equipment and technique described above, 114 g. of compound II was added to a solution of 300 g. of potassium hydroxide in 700 cc. of water. Upon cooling, a small flash occurred in the vent line; 27.4 g. of material with the following properties was recovered from the traps.

	Unknown	Reported for 1,1-dichloroethylene
Boiling point, °C.	30.5	31.6
Density { g./cc.	1.168	1.218
°C.	25	20
n_D^{20}	1.4253	1.4270

The reactions observed here may be formulated in steps as exemplified below for the reaction of β,β -dichlorovinyltrichlorosilane.



The first step is an attack of hydroxyl ion on silicon to give the carbanion, $^-CH=CCl_2$, which may stabilize itself by reaction with the solvent, reac-

(2) Krieble and Elliott, *ibid.*, **67**, 1810 (1945).

tion (2), or by loss of a chloride ion by reaction (3) to give chloroacetylene.

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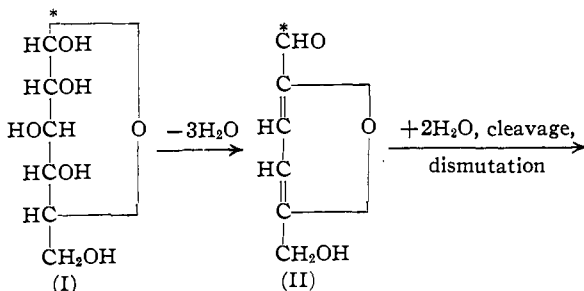
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The Action of Hydrobromic Acid on 1-C¹⁴-D-Glucose

BY JOHN C. SOWDEN

The dehydration and cleavage of D-glucose by vigorous treatment with mineral acids was first studied by Grote and Tollens¹ who recognized the principal products of the reaction as levulinic acid and formic acid, which are formed along with varying amounts of highly colored polymeric "humins." Earlier, Mulder² had obtained formic acid from the action of sulfuric acid on sucrose and undoubtedly the other product he obtained, "glucinic acid," was in reality levulinic acid, later purified, characterized and renamed by Grote and Tollens.³

The mechanism of the reaction remained obscure until comparatively recent times: 5-Hydroxymethyl-2-furaldehyde was recognized as a probable intermediate by Kiermayer⁴ and by van Ekenstein and Blanksma.⁵ Following a critical study of the reaction, Pummerer and co-workers⁶ concluded that 5-hydroxymethyl-2-furaldehyde (II) is first formed from the hexose (I) with the loss of three molecules of water and that this intermediate then undergoes hydration, cleavage and dismutation to produce levulinic and formic acids (III).



According to this proposed mechanism, the aldehyde carbon of the hexose eventually becomes the carbon of the resultant formic acid. This latter assumption has now been substantiated by an examination of the products from 1-C¹⁴-D-glucose⁷ and hydrobromic acid: The levulinic acid produced was devoid of radioactivity whereas the formic acid showed quantitatively the radioactivity previously possessed by the aldehyde carbon of the glucose.

- (1) Grote and Tollens, *Ann.*, **206**, 226 (1880).
- (2) Mulder, *J. prakt. Chem.*, **21**, 229 (1840).
- (3) Grote and Tollens, *Ber.*, **7**, 1375 (1874).
- (4) Kiermayer, *Chem. Z.*, **19**, 1004 (1895).
- (5) van Ekenstein and Blanksma, *Ber.*, **43**, 2355 (1910).
- (6) Pummerer and Gump, *ibid.*, **56**, 999 (1923); Pummerer, Guyot and Birkofer, *ibid.*, **68**, 480 (1935).
- (7) Sowden, *Science*, **109**, 229 (1949).

Experimental

One gram of 1-C¹⁴-D-glucose, showing radioactivity of 860 = 20 c.p.m./mg., was heated with 10.0 cc. of 10% hydrobromic acid in a sealed tube at 130° for twenty-four hours.⁸ The resulting slight precipitate of "humins" was filtered off and washed. Sufficient sodium hydroxide solution was then added to the filtrate to exactly neutralize the hydrobromic acid. The resulting solution was distilled to dryness, using an oil-bath, and water was added and the distillation repeated twice.

The residue was extracted with anhydrous ether and the extract concentrated. The residual liquid, on treatment with phenylhydrazine, yielded 0.55 g. (48%) of *non-radioactive* levulinic acid phenylhydrazone, m. p. after recrystallization 109–110°.⁹

The distillate from the reaction mixture was titrated with 0.1 N sodium hydroxide solution to neutralize the distilled formic acid, requiring 44.7 cc. (80%) to the methyl red end-point. The resulting sodium formate was converted to *p*-phenylphenacyl formate, m. p. after recrystallization 74–75°.¹⁰ This product when counted in the same manner⁷ as the original 1-C¹⁴-D-glucose showed radioactivity of 650 = 20 c.p.m./mg. On the assumption that the formic acid was produced from the aldehyde carbon of the D-glucose the predicted radioactivity was 645 = 20 c. p. m./mg.

(8) Ploetz, *Naturwiss.*, **29**, 707 (1941).

(9) Fischer, *Ann.*, **236**, 146 (1886).

(10) Drake and Bronitsky, *THIS JOURNAL*, **52**, 3715 (1930).

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An Antistine Intermediate

BY ARTHUR J. TOMISEK¹

This synthesis of (N-phenyl-N-benzylglycyl)-2'-aminoethylamide, Ph(PhCH₂)NCH₂-CONHCH₂CH₂NH₂, represents an abandoned project in which it was desired to test a synthetic route leading to compounds of antistine-like structure.

Ethyl N-Benzyl-N-phenylglycinate.—Twenty-one and two-tenths grams (0.116 mole) of benzylaniline² and 6.42 ml. (0.058 mole) of ethyl bromoacetate in a stoppered flask were heated in a 45° oven for twenty hours. The pasty product was churned for two hours with 585 ml. of 0.3 N hydrochloric acid (0.174 mole) in order to extract unreacted benzylaniline. The viscous, semi-crystalline phase was crude ethyl N-benzyl-N-phenylglycinate hydrochloride. This was an unstable product, and was therefore dried in a desiccator and used directly in the next step.

(N-Phenyl-N-benzylglycyl)-2'-aminoethylamide.—The crude ethyl N-phenyl-N-benzylglycinate and 35 ml. of ethylenediamine (95–100%) were refluxed for five hours, cooled and poured into water. The oily phase was extracted with methylene chloride, washed with water and dried over sodium sulfate. Solvent was removed on a steam-bath and the residue was crystallized and recrystallized from anhydrous butanol-ethanol-hydrogen chloride. The white powder separated very slowly. It was characterized by the benzaldehyde odor and the intense red color which result from its contact with strong nitric

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(2) Willson and Wheeler, "Organic Syntheses," Coll. Vol. I, 102 (1941).