acid had aged forty-eight hours and ten days. Freshly prepared ferric chloride solutions were used in each case. The results indicated strongly that the activity of the acid decreased with age. The greatest increase in hydrogen ion concentration occurred with the freshly prepared acid. Similarly, the discharge in color of the ferric ion occurred to the greatest extent with this system. As the sol was aged, the molecular weight of the silicic acid increased. The sol was clear in reflected light when fresh. It was mildly opalescent at ten days and it gelled within seventeen days.

It is generally conceded that the increase in molecular weight on aging is due to polymerization:

$$2{\equiv}\text{Si—OH} \longrightarrow {\equiv}\text{Si—O—Si}{\equiv} + \text{H}_2\text{O}$$

Since the occurrence of this change decreases the reactivity of the acid, it may be suggested that the H atom in the structure $\equiv$Si—OH is the source of H^+ ions. Neglecting the hydration of the ferric ion, the following reaction may be written to account for the increase in hydrogen ion concentration.

$$n{\equiv}\text{Si—OH} + \text{Fe}^{+++} \longrightarrow [({\equiv}\text{Si—O})_n\text{—Fe}]^{(3-n)+} + n\text{H}^+$$

Alternatively the reactions may consist of

$$\text{Fe}^{+++} + \text{H}_2\text{O} \rightleftarrows \text{FeOH}^{++} + \text{H}^+$$

and

$${\equiv}\text{Si—OH} + \text{HOFe}^{++} \longrightarrow {\equiv}\text{Si—O—Fe}^{++} + \text{H}_2\text{O}$$

The latter reaction is in accord with the fact that silicates are capable of discharging the color of iron in alkaline solution.

These studies are being continued.

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5-Chlorofurfuryl Derivatives

BY F. A. HOCHSTEIN AND GEORGE F WRIGHT

We wish to report a contrast in stability between two 5-chlorofurfuryl derivatives, the alcohol and the amine.

The preparation of 5-chlorofurfuryl alcohol resembles that of the bromo analog.[1] When peroxide[2] was present the Cannizzaro reaction with 5-chlorofurfural[3] gave a high yield of 5-chlorofuroic acid, but the yield of 5-chlorofurfuryl alcohol was low because of spontaneous decomposition, and a tendency to co-distil with solvent ether. Like other *alpha* halogenated furans with saturated substituents it was unstable in the pure state, though it did not decompose in boiling ethanol after many hours.

By contrast 5-chlorofurfurylamine is quite stable in the pure state over a long period of time. It was kept for several years, following its preparation by acid–sodium amalgam reduction of 5-chlorofurfuraldoxime. We suggest that this amine is more stable than the alcohol because it can neutralize traces of acid decomposition products, and thus retard auto-decomposition.

Experimental[4]

5-Chlorofurfuryl Alcohol.—A solution of 30 g. (0.23 mole) of 5-chlorofurfural (3) in 100 cc. of ether was stirred vigorously at 20–30° for four to seven days with 750 cc. (5 moles) of 30% aqueous sodium hydroxide. It was usually unnecessary to add hydrogen peroxide because the stock ether and the alkali contained sufficient of this catalyst. There was no apparent temperature rise. When the etherous layer no longer gave a test with 2,4-dinitrophenylhydrazine reagent, about 800 cc. of water was added to dissolve the sodium 5-chloro-2-furoate. The aqueous layer, after separation, was extracted five times with ether.

The combined ether extract was washed successively with water, then with saturated aqueous solution of sodium bisulfite and ferrous sulfate solution, and finally with water. After drying with magnesium sulfate the solution was treated with a measured excess of ethyl bromide Grignard reagent. The ether was distilled from the Grignard complex under vacuum. After several hours the residue was hydrolyzed with that amount of acetic acid in ice which is equivalent to the titer of the Grignard reagent which was added. The oil which separated was taken up in half its volume of butene-2, dried with calcium chloride and distilled under 10 mm. pressure with an ice water-bath as the heat source. Addition of butene-2 and subsequent distillation was twice repeated.

The residual oil was dissolved in commercial pentane (b.p. 26–30°) at 0° under nitrogen, cooled to −80° and the supernatant liquor removed with a filter stick. The 2 g. of long white needles remaining after seven such crystallizations melted at 16–17°, yield 30% of theoretical. This could be distilled at 46–47° (3×10^{-4} mm.) into a cold receiver. The compound decomposes violently in concd. sulfuric acid. When a 10% solution of pure 5-chlorofurfuryl alcohol in absolute ethanol was boiled thirteen hours the recovery of 5-chlorofurfuryl alcohol was nearly quantitative.

Anal. Calcd. for $C_5H_5O_2Cl$: C, 45.3; H, 3.80; Cl, 26.8. Found: C, 44.7; H, 3.68; Cl, 26.7.

5-Chlorofurfuryl Trityl Ether.—A solution of 2.1 g. (0.016 mole) of 5-chlorofurfuryl alcohol in 20 cc. of dry pyridine was treated with 4.5 g. (0.016 mole) of trityl chloride. After one day the system was diluted with water to 30 cc. The solid mass was fractionally crystallized from petroleum ether (b.p. 60–70°) to give the less soluble trityl alcohol and a more soluble fraction. The latter was thrice crystallized from ethanol after which it melted at 100.5–102°, wt. 1 g. (16% of theoretical). It could also be crystallized from methanol and from petroleum ether (b. p. 26–30°).

Anal. Calcd. for $C_{24}H_{17}O_2Cl$: C, 76.9; H, 5.11. Found: C, 76.8; H, 5.30.

5-Chlorofurfurylamine.—A solution of 7.25 g. of 5-chlorofurfuraldoxime[5] in 100 cc. of 95% ethanol was stirred for one hour while 237 g. of 2.5% sodium amalgam and 15.5 g. of acetic acid were added proportionately. The diluted acidic solution, after ether extraction, was made basic and again extracted with ether. The latter extract (dried with sodium sulfate) was distilled, finally at 50–55° (25 mm.). The yield of 5-chlorofurfurylamine was 5.0 g. or 76% of theoretical. The compound was converted to the chloroplatinate for analysis.

Anal. Calcd. for $C_5H_6ONCl{\cdot}H_2PtCl_6$: Pt, 29.0. Found: Pt, 29.0.

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(1) W. J. Chute, W. M. Orchard and G. F. Wright, *J. Org. Chem.*, 6, 157 (1941).

(2) M. S. Kharasch and M. Foy, THIS JOURNAL, 57, 1510 (1935).

(3) W. J. Chute and G. F Wright, *J. Org. Chem.*, 10, 541 (1945).

(4) All melting points have been corrected against known standards.

(5) H. Gilman and G. F Wright, *Rec. trav. chim.*, 50, 833 (1931).

When the amine was boiled twelve hours in ethanol the recovery of material was quantitative and its chloroplatinate contained 29% of platinum.

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3-Benzyl-5,5-dimethylhydantoin

BY T. EARL JORDAN AND SARA GINSBURG[1]

3-Benzyl-5,5-dimethylhydantoin was prepared by treating benzyl chloride with 5,5-dimethylhydantoin. It was found that this compound would neither hydrolyze to the corresponding amino acid nor react with acetic anhydride under conditions which usually effect such reactions of substituted hydantoins. This stabilizing effect of the benzyl group was unexpected.[1a,2,3]

Experimental

The 5,5-dimethylhydantoin was prepared by a modification of the method of Bucherer and Libe.[4] A mixture of acetone, sodium cyanide and ammonium hydroxide (mole ratio of 1:1.2:1.35) was agitated with carbon dioxide in an autoclave at 150–200 lb. gage pressure and 80 ± 5° until adsorption ceased. The solvent medium was 50% ethanol–water solution sufficient to equal two and one-half times the weight of the reactants. The by-product sodium bicarbonate was filtered off, washed with alcohol; the filtrate and washings were combined, distilled until practically free of alcohol; the residue was treated with hydrogen peroxide to destroy any unreacted sodium cyanide, neutralized with dilute sulfuric acid and cooled. 5,5-Dimethylhydantoin was filtered off and recrystallized from water; yield, 82%; colorless needles, m. p. 175°.

3-Benzyl-5,5-dimethylhydantoin was obtained by treating 5,5-dimethylhydantoin with benzyl chloride in the presence of sodium bicarbonate (mole ratios of 1:1.3:1.4). Three hours were required for the addition of benzyl chloride; the refluxing and agitation were continued for five hours longer. On cooling, an oily solid precipitated. This was neutralized, filtered and recrystallized from 30% alcohol; yield, 80%; white needles, m. p. 106° (cor.).

Anal. Calcd.: C, 66.06; H, 6.42; N, 12.84. Found: C, 65.9; H, 6.6; N, 12.7. Solubility in H_2O: at 20°, 0.35 g. in 100 ml.; at 100°, 1.37 g. in 100 ml.; in boiling 50% alcohol, 100 g. in 100 g.; in boiling 30% alcohol, 20 g. in 100 g.

Attempts to hydrolyze the 3-benzyl-5,5-dimethylhydantoin with 60% sulfuric acid by refluxing for twenty-three hours resulted in practically no reaction. Refluxing with 80% sulfuric acid for ten hours resulted in a tar only.

Refluxing 3-benzyl-5,5-dimethylhydantoin for four hours with a large excess of acetic anhydride and a trace of concentrated sulfuric acid resulted in no reaction.

(1) Present address: Physicians Drug & Supply Co., Philadelphia, Pa.

(1a) H. L. Dakin, *J. Biol. Chem.*, **44**, 518 (1920).

(2) W. Robson, *ibid.*, **62**, 495 (1924).

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The Relative Efficiency of Various Surfaces for the Recombination of Hydrogen Atoms

BY SIDNEY KATZ, G. B. KISTIAKOWSKY AND ROBERT FRANK STEINER

An investigation has been made of the relative efficiency of various metallic surfaces in promoting the recombination of hydrogen atoms.

The steady-state temperature rise produced in the catalyst by the heat of recombination was taken as a measure of the relative effectiveness. Atomic hydrogen was produced by a 5000-volt a. c. discharge. A flow system was utilized, with hydrogen from a high pressure cylinder diffusing into the discharge tube through a long glass capillary. The pressure of hydrogen at one end of the capillary was maintained effectively constant by means of a mercury overflow bottle. Prior to entering the capillary, the hydrogen was bubbled through a dilute solution of sulfuric acid, to ensure the presence of sufficient moisture to inhibit atomic recombination on the walls.

Hydrogen, after leaving the discharge tube, streamed by the catalyst cone, which fitted over a glass thermocouple well, blown into the wall of the system and projecting into the center of hydrogen flow. Temperature rise was recorded by means of a copper–constantan thermocouple, one junction of which was inserted in the thermocouple well and the other immersed in an ice–water-bath. Measurements were made with a Leeds and Northrop student potentiometer. All readings were recorded in microvolts.

The catalyst cones were introduced into a separately evacuable chamber, placed above the thermocouple well, which was then closed and evacuated. It was separated from the hydrogen flow system by a large bore stopcock. The cones, suspended by threads, were lowered by means of a winch upon the thermocouple well, through the bore of the large stopcock. This arrangement permitted an interchange of catalyst cones without interruption of hydrogen flow or the electric discharge. The cones were turned from

TABLE I

Surface	$V_{\text{final}} - V_{\text{initial}} = \Delta V$ (microvolts) (average values)	$-\Delta V/\Delta V_{\text{cobalt}}$
	Run I	
Cobalt	1041	1.00
Nickel	950	0.91
Copper	767	.74
Chromium	735	.71
Brass	756	.73
Zinc	342	.33
Tin	90	.09
Cadmium	698	.67
Paraffin	240	.23
	Run II	
Cobalt	447	1.00
Nickel	410	0.92
Copper	312	.70
Zinc	146	.33
Brass	280	.63
	Run III	
Cobalt	696	1.00
Platinum	710	1.02
Iron	578	0.83