Experimental[4]

3,4,5-Trimethoxyacetophenone.—In accordance with the directions of Hauser[2] we obtained 29.8 g. of the ketone, m. p. 72–74°, from 46.0 g. of the corresponding acid chloride (yield, 71%). After further recrystallization from benzene–ligroin the melting point was raised to 79–81°.

β-Piperidyl-3,4,5-trimethoxypropiophenone Hydrochloride.—A mixture of 26.3 g. of the above ketone, 15.3 g. of piperidine hydrochloride, 5.6 g. of paraformaldehyde and 37.5 ml. of absolute ethanol containing 0.25 ml. of concentrated hydrochloric acid was heated under reflux for one hour. Then 3.8 g. of paraformaldehyde was added and heating continued for an additional two hours. The hot mixture was treated with 300 ml. of acetone, refluxed for fifteen minutes, cooled and filtered. There was obtained 30.3 g. (71%) of the desired salt. The analytical sample, which was crystallized twice from absolute ethanol–ether, melted at 194.4–195.2° (cor.).

Anal. Calcd. for $C_{17}H_{25}NO_4 \cdot HCl$: C, 59.38; H, 7.62; N, 4.07. Found: C, 59.29; H, 7.42; N, 3.98.

β-Dimethylamino-3,4,5-trimethoxypropiophenone Hydrochloride.—When an equivalent quantity of dimethylamine hydrochloride was substituted for the piperidine hydrochloride in the above experiment, the corresponding salt was obtained in 71% yield. Two recrystallizations from dry ethanol–ether gave the pure product, m. p. 174.5–175.3° (cor.).

Anal. Calcd. for $C_{14}H_{21}O_4N \cdot HCl$: C, 55.34; H, 7.30; N, 4.61. Found: C, 55.31; H, 7.25; N, 4.74.

β-Diethyl-3,4,5-trimethoxypropiophenone Hydrochloride.—This salt was obtained in 66% yield when diethylamine hydrochloride was used in the above procedure. The pure compound was obtained after two crystallizations from alcohol–ether; m. p. 144.8–146.5° (cor.).

Anal. Calcd. for $C_{16}H_{25}O_4N \cdot HCl$: C, 57.91; H, 7.90; Cl, 10.68. Found: C, 58.00; H, 8.02; Cl, 10.66.

β-(3,4,5-Trimethoxybenzoyl)-propionitrile.[5]—A solution of 60.6 g. of β-diethylamino-3,4,5-trimethoxypropiophenone hydrochloride, 15.2 ml. of concentrated hydrochloric acid and 1900 ml. of water was heated and stirred under reflux while 47.6 g. of potassium cyanide dissolved in 180 ml. of water was added beneath the surface of the liquid over a twenty-minute period. After one hour the mixture was cooled and the solid collected. The product from two such runs was crystallized from dilute ethanol to give the nitrile, m. p. 115–116.5°; yield, 65%. A small sample was crystallized from ethanol and analyzed; m. p. 115.5–116.5°.

Anal. Calcd. for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07. Found: C, 62.99; H, 6.08.

β-(3,4,5-Trimethoxybenzoyl)-propionic Acid.—A mixture of 12.5 g. of the nitrile, 12.0 ml. of ethanol and 5.5 ml. of sulfuric acid was refluxed for sixteen hours and poured onto ice-water. The mixture was made slightly basic and the solid ester collected. It was refluxed for four hours with 10% sodium hydroxide. The mixture was diluted with an equal volume of water, acidified with hydrochloric acid and cooled. After several hours in the ice-chest, the acid was collected on a filter and dried; wt. 9.9 g. (66%). After crystallization from benzene the product melted at 120–121°. (Haworth[1] reported 121–122° as the melting point for the acid.)

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[4] The analyses were carried out under the supervision of Mr. M. E. Auerbach.

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Interaction of Ferric Ions with Silicic Acid

BY FRED HAZEL, RICHARD U. SCHOCK, JR., AND MAXWELL GORDON

Application of synthetic base exchange resins to the preparation of colloidal silicic acid[1] provides a method for obtaining this system in a pure form without resorting to prolonged dialysis. The saving in time affords a particular advantage in the case of silicic acid sols because the superposed aging with condensation to larger particles is avoided. It is clear that the use of freshly prepared systems gives a favorable opportunity for studying the reactions of the acid.[2]

Silicic acid sols containing 2.5 ± 0.1% silica were prepared by adding measured volumes of diluted sodium silicate to weighed portions of ion exchange resins in the hydrogen form as described previously.[2] The silicate had a sodium oxide–silica ratio by weight of 1:3.2 and was a standard commercial product ("E brand") of the Philadelphia Quartz Company.

Freshly prepared solutions of various salts were titrated with the freshly prepared acids. Changes in hydrogen ion concentration were followed with Leeds and Northrup *p*H meters employing glass electrodes. Preliminary experiments were carried out with barium chloride, lanthanum chloride, copper sulfate, chromic chloride, aluminum sulfate, aluminum chloride and ferric chloride. The first three salts gave no indication of interaction while that with chromic chloride was slight. Aluminum chloride and ferric chloride showed the greatest interaction.

Results obtained on mixing two volumes of silicic acid sol and one volume of various salt solutions are given in Table I.

TABLE I

INTERACTION OF COLLOIDAL SILICIC ACID WITH METALLIC IONS

*p*H silicic acid	Salt, *M*		Original *p*H	Final *p*H	Change in hydrogen ion concentration, *M*
2.21	0.1	$FeCl_3 \cdot 6H_2O$	1.77	1.70	0.003
2.21	.05	$FeCl_3 \cdot 6H_2O$	1.97	1.83	.004
2.21	.025	$FeCl_3 \cdot 6H_2O$	2.12	1.95	.0036
2.97	.2	$AlCl_3 \cdot 6H_2O$	3.07	2.52	.0021
3.20	.02	$AlCl_3 \cdot 6H_2O$	3.46	2.71	.0016
3.27	.1	$Al_2(SO_4)_3 \cdot 18H_2O$	3.02	2.87	.00044
3.27	.01	$Al_2(SO_4)_3 \cdot 18H_2O$	3.42	2.95	.00072
3.23	.02	$CrCl_3 \cdot 6H_2O$	3.30	3.17	.00018

The interaction with ferric chloride was manifest not only by the considerable increase in hydrogen ion concentration but also by the discharge of the color of the solution of ferric salt. Control experiments were carried out substituting various strong mineral acids for silicic acid, and these showed clearly that the reaction was due to silicic acid.

Additional experiments were conducted with a silicic acid sol prepared by mixing hydrochloric acid and sodium silicate.[3] This system also had a concentration of 2.5% silica and a *p*H of 2.2. The freshly prepared acid was used to titrate ferric chloride solutions of different concentrations. Titrations were repeated after the silicic

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[1] Bird, U. S. Patent 2,244,325, June 3, 1941.

[2] Hazel, *J. Phys. Colloid Chem.*, **51**, 415 (1947).

[3] Graham, *Pogg. Ann.*, **114**, 187 (1861).

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:

$$2{\equiv}\mathrm{Si{-}OH} \longrightarrow {\equiv}\mathrm{Si{-}O{-}Si}{\equiv} + \mathrm{H_2O}$$

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.

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

Alternatively the reactions may consist of

$$\mathrm{Fe^{+++}} + \mathrm{H_2O} \rightleftharpoons \mathrm{FeOH^{++}} + \mathrm{H^+}$$

and

$${\equiv}\mathrm{Si{-}OH} + \mathrm{HOFe^{++}} \longrightarrow {\equiv}\mathrm{Si{-}O{-}Fe^{++}} + \mathrm{H_2O}$$

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).