their method has been applied to column chromatography, using a cellulose product (Solka-Floc BW100, supplied by the Brown Company, Berlin, N. H.) and alcohols of different chain length. The order of emergence of the keto-acid derivatives agrees with the R_f values obtained by Cavallini, *et al.*[3] As the R_f values increase longer alcohol chains are needed for adequate resolution.

One to two grams of Solka-Floc was suspended in ammonia saturated *n*-amyl alcohol and introduced into a glass tube of 30-cm. length and 0.6-cm. diameter, the tip of which was plugged with a tuft of cotton. After the column had settled, 0.1 to 0.4 mg. of the hydrazones dissolved in 0.2 ml. of *n*-butanol or ethyl ether were introduced. As soon as the solution had entered the column completely the eluant was added. For satisfactory results, excess moisture must be avoided. Effluent fractions of 0.70 ml. per tube collected on a Technicon collector were diluted to 3.70 ml. with *n*-butanol, then hydrazone concentrations were measured by a Beckman spectrophotometer at 380 mμ. This method of reading hydrazone concentrations at this wave length was found to be not only simpler but 1.5 times more sensitive than alkalization and reading in the visible range.[2] Also, the color of the hydrazones in the butanol diluent was stable for several hours. Whenever there was present any free 2,4-dinitrophenylhydrazine in the sample, the acids were extracted into an ethyl ether and 0.2 ml. was placed on the column in order to effect an adequate separation of the reagent from the hydrazones.

Figure 1 shows the separation of pyruvic, oxalacetic and α-ketoglutaric acid hydrazones, using *n*-amyl alcohol saturated with ammonia as eluant. Figure 2 shows that of pyruvic, α-ketobutyric, and α-keto-γ-methiolbutyric acid hydrazones, using *n*-decyl alcohol saturated with ammonia as eluant.

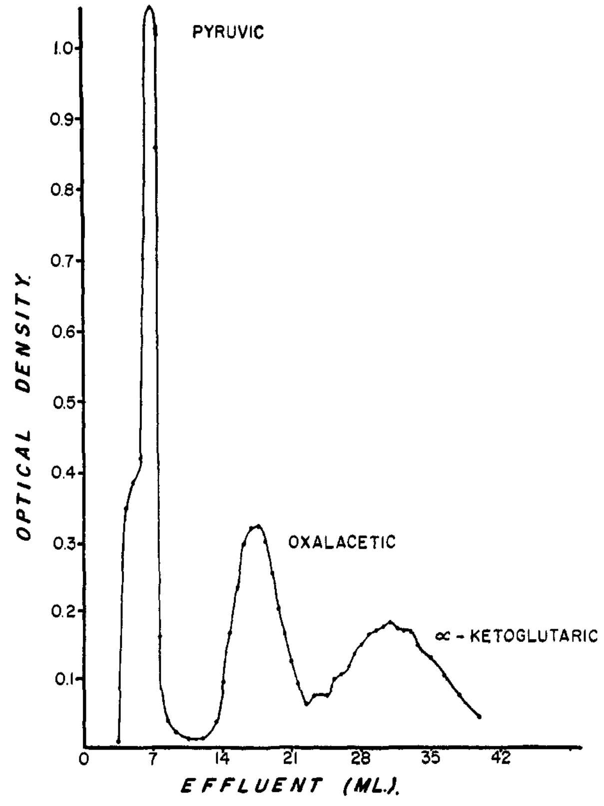

Fig. 1.—Chromatograph of pyruvic, oxalacetic and α-ketoglutaric acid hydrazones.

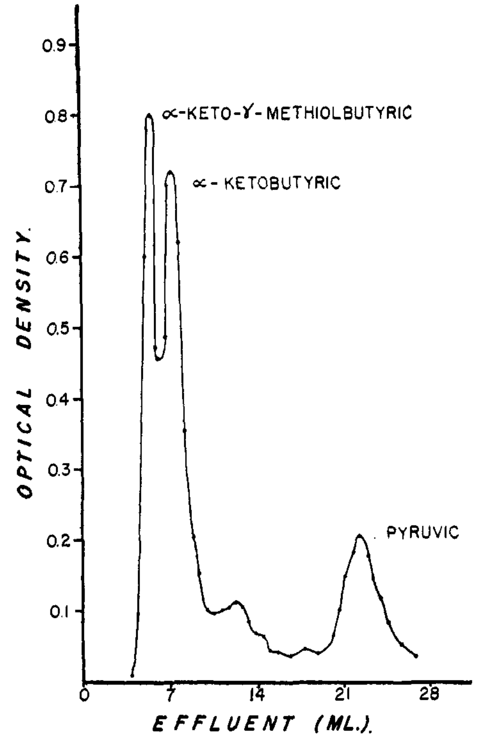

Fig. 2.—Chromatograph of pyruvic, α-ketobutyric and α-keto-γ-methiolbutyric acid hydrazones.

It was found that in conditions of best resolution, there was a separation of the pyruvic acid hydrazone into two bands, as reported by LePage.[2] All five acids may be separated on one chromatographic run by the use of a developing liquid delivered from a reservoir so arranged that the *n*-butyl-*n*-decyl alcohol mixture will gradually and automatically increase with respect to the concentration of the *n*-butyl alcohol.[4] The acids emerge in the following order: γ-methiol-α-ketobutyric, α-ketobutyric, pyruvic, oxalacetic and α-ketoglutaric. By this method, recovery of the hydrazones ranged from 75 to 90%, being highest for the pyruvic acid hydrazone. For identification, the emerging hydrazones were mounted on NaCl crystals and examined in the infrared spectrum between 1800 and 1400 cm.$^{-1}$

[4] K. Donaldson, V. Tulane and L. M. Marshall, *Anal. Chem.* (in press).

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The Photochemical Chlorination of Methylsilicones

BY J. R. ELLIOTT AND E. M. BOLDEBUCK

The photochemical reaction of ferric chloride with organic materials such as alcohols,[1] acids,[2] al-

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[1] M. Prasad and P. S. Limaye, *J. Indian Chem. Soc.*, **10**, 91, 101 (1933).

[2] J. C. Ghosh and R. M. Purakayastha, *ibid.*, **6**, 827 (1929).

dehydes[3] and ethers,[3,4] has been described. In the case of ethyl ether,[4] the products of reaction are reported to include ferrous chloride dihydrate, di- and trichlorinated ether, and polymeric aldehydes.

We have found that methylsilicone solutions of anhydrous ferric chloride are stable in the dark but immediately reactive in sunlight. In an illuminated hexamethyldisiloxane solution, ferric chloride is converted completely to ferrous chloride. Half the chlorine available from the reduction of ferric chloride appears as hydrolyzable chlorine; the second half is non-hydrolyzable. Reaction products identified include hydrogen chloride, trimethylchlorosilane, water and chloromethylpentamethyldisiloxane. These products can all be accounted for if one assumes chlorination of a methyl group accompanied by formation of hydrogen chloride. Attack of the siloxane bond by hydrogen chloride would produce a chlorosilane and a silanol; water would then be formed by subsequent condensation of silanols.

Experimental

Procedure.—A weighed portion of reagent grade iron wire was quantitatively converted to ferric chloride by reaction with chlorine in a dry vacuum system, and was sublimed under chlorine into a Pyrex reaction tube. A weighed amount of previously degassed hexamethyldisiloxane was then distilled directly into the reaction tube. A portion of the resulting yellow solution appeared unchanged after standing two weeks in the dark.

The yellow solution, generally containing undissolved ferric chloride, was illuminated with a General Electric H-6 water-cooled mercury capillary arc until both the solution and the solid were colorless. The liquid product was then separated from the solid residue by vacuum distillation at room temperature. When the solid appeared dry, the system was brought to atmospheric pressure with dry nitrogen.

Analysis of Volatile Products.—Mass spectrometer analysis of various fractions of the volatile products of one run indicated that at liquid nitrogen temperature, no non-condensable gases except a trace of nitrogen were present; at room temperature hexamethyldisiloxane, trimethylchlorosilane and hydrogen chloride were indicated. Analysis of various fractions of the liquid by mass spectrometer and infrared absorption gave no indication of molecules containing C–C bonds.

Chlorine analyses from two preparations are listed in Table I.

TABLE I

DISTRIBUTION OF CHLORINE IN PRODUCTS

Prep. No.	Initial mole $FeCl_3$	Mole siloxane	Time of illum.	Mole hydrol. chlorine	Mole non-hydrol. chlorine
A	0.0013	0.45	45 min.	0.00062	....
B	.016	.69	6 hr.	.0078	0.0078

The distillate from A was hydrolyzed in an ether–ice mixture and titrated for acid directly. Distillate from B was hydrolyzed and washed with ice-water until the washings were neutral. Acid content of the aqueous phase was determined by titration. All chlorine originally present as hydrogen chloride or chlorosilane was thereby determined as aqueous hydrochloric acid.

Water-insoluble liquid from B was distilled in a small fractionating column of about 10 plates to remove unreacted hexamethyldisiloxane, boiling at 100°. A portion of the liquid residue, which contained undistilled hexamethyldisiloxane and a chlorinated material, was analyzed for chlorine by Parr bomb fusion. A micro-boiling point measurement of the residue reached a constant temperature at 150°, indicating the presence of chloromethylpentamethyldisiloxane (b.p. 152°). Since the silicon–carbon bond of chlorinated methyldisiloxanes is readily cleaved by alkali to give the corresponding chloromethanes,[5] the residue was heated at 80° with potassium hydroxide pellets. The exit gases were condensed in a Dry Ice, acetone-cooled trap; and were examined in the mass spectrometer. All possible fragments of methyl chloride were identified and, in addition, a trace of hexamethyldisiloxane; no di- or trichlorinated carbon derivative was found. It was thus assumed that the non-hydrolyzable chlorine was present exclusively in chloromethylpentamethyldisiloxane.

Analysis of Residue.—Aqueous solutions of the light gray, powdery residue gave strong tests for ferrous and chloride ions, a faint test for ferric ion. Iron content of the salt, after oxidation by bromine, was determined colorimetrically in 30% HCl at 4200 Å. by the use of the Beckman spectrophotometer. Chlorine was determined by the Volhard method.

Water content of the residue from B was determined by heating a portion of the residue to 200° in a stream of dry hydrogen chloride. Exit vapors were passed through a Dry Ice–acetone-cooled trap and the condensate was examined for water by the Karl Fischer method. Water content of the original hexamethyldisiloxane used in the reaction was less than 1% of that found in the products.

Results of analyses of the residue from preparations A and B are listed in Table II.

TABLE II

ANALYSES OF SOLID RESIDUE

Prep. No.	Iron, %	Chlorine, %	Wt. loss at 200°, %	H_2O, %	Calculated formula
A	38.6	49.3	..	...	$FeCl_{2.01}$
B	39.3	50.3	10.9	2.4	$FeCl_{2.02} \cdot 0.18H_2O$

A portion of the residue from preparation A was heated at 100° in the vacuum system at 10^{-4} mm. pressure. The small amount of distillate was composed of water and a carbon tetrachloride soluble phase. Examination of the carbon tetrachloride solution by infrared absorption showed no evidence of C–C bonds, but over the limited range of measurement gave the absorption curve of hexamethyldisiloxane.

Influence of Oxygen.—Sixty-five grams of a 1 mole % suspension of ferric chloride in hexamethyldisiloxane was prepared in the vacuum system as described above and dry oxygen was bubbled through the solution during a 40-minute period of illumination. Exit gases, which were collected in a liquid nitrogen-cooled trap, had a strong formaldehyde odor. Contents of the trap were dissolved in water and examined for formaldehyde by the standard hydrogen peroxide method.[6] A total of 5 mg. of formaldehyde was found.

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[3] A. Benrath, *J. prakt. Chem.*, [2] **72**, 220 (1905).

[4] E. Puxeddu, *Gazz. chim. ital.*, **50**, 153 (1920).

[5] R. H. Krieble and J. R. Elliott, THIS JOURNAL, **68**, 2291 (1946).

[6] J. Assoc. Official Agr. Chem., Methods of Analysis, p. 75 (1916).

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Chain Transfer of Styrene with Various Dihalides and the Preparation of Polystyrene Dihalides

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One method for preparing chain molecules of low or intermediate molecular weight terminated on both ends by a halogen atom is to carry out a vinyl or diene polymerization in the presence of a dihalide which acts as a chain transfer agent. The polymeric dihalides thus produced (whose formula in a simple case would be $X(CH_2CHY)_nX'$) can