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

BY J. A. GANNON, E. M. FETTES AND A. V. TOBOLSKY

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 then be used in further polymerizations, as for example in a polysulfide condensation. In all cases a heterogeneous distribution of molecular weights is obtained in the preparation of the polymeric dihalides which in the simplest case would be a "random" distribution.[1,2]

The most desirable chain transfer agent to be used in this connection is one whose chain transfer constant is close to unity. In this case the number average and weight average molecular weights should be approximately independent of conversion and the distribution of molecular weights at high conversion should be much less heterogeneous than is the case when the chain transfer constant differs appreciably from unity.

We investigated numerous dihalides as chain transfer agents for styrene polymerization in an attempt to select several whose chain transfer constants were close to unity. The data for chain transfer constant were obtained in most cases at 60° and in some cases at 80°. The experimental procedure used was identical with that reported by Gregg and Mayo[3,4] using intrinsic viscosity to obtain number average degree of polymerization.

To check our experimental accuracy we redetermined the values for the chain transfer constant of carbon tetrachloride with styrene at 60°. Our value was 0.0087 compared with the Gregg–Mayo value[3] of 0.0093.

The following observations should be pointed out: (1) In using the Gregg–Mayo method, it is very necessary to produce polymers of very low conversion. (2) In certain cases we used thermal initiation and in other cases we used benzoyl peroxide as an initiator. The results are independent of the form of initiation. (3) When large quantities of the most active dihalides were used an important retardation of polymerization was observed in the presence or absence of catalyst. (4) The molecular weight distributions to be expected when symmetrical dihalides are used as transfer agents is different from the simpler case when one halogen atom is very active to chain transfer and the other is relatively inert. (5) When dichlorides are used as the transfer agent we believe that very often hydrogen atoms rather than chlorine atoms are abstracted which, of course, does not produce polymers with a chlorine atom at each end. On the other hand, when dibromides or diiodides are used, polystyrene molecules are formed with a bromine or iodine atom at each end. (6) A certain fraction of the chains, corresponding to those that were initiated by catalyst fragments, or possibly by the thermal initiation, have bromine or iodine atoms at only one end. This fraction is small when active chain transfer agents are used in large concentrations. (7) At high conversions important transfer occurs with the halide terminated polymer as well as with the original dihalide molecules.

Table I shows the chain transfer constants for various purified dihalides with styrene obtained under the indicated conditions.

The results indicate that for comparable molecules iodides are more active than bromides and bromides more active than chlorides. Allylic or benzylic halides are exceptionally active, which has been previously noted for hydrocarbons.[4] The halogen atom on an acid halide is also extremely active.

TABLE I

CHAIN TRANSFER CONSTANTS FOR STYRENE WITH VARIOUS DIHALIDES

Dihalide	Temp., °C.	Weight % benozyl peroxide	Chain transfer constant
Bischloroethylformal	80	0.0165	0.00060
Methylene dichloride	80	.0165	.00095
Ethylene dichloride	80	.0165	.00098
1,4-Dichlorobutene-2	80	.0165	.0051
Chloroacetyl chloride	60	None	.330
Methylene dibromide	60	None	.011
p-Xylylene dibromide	60	None	.015
Styrene dibromide	60	None	.195
Stilbene dibromide	60	None	.302
Bromoacetic acid[b]	60	None	.043
Acetyl bromide[a,b]	60	None	.86
Methylene diiodide	60	None	.071

[a] Value somewhat uncertain due to partial hydrolysis.
[b] Monohalides.

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Reduction of an Amidine with Lithium Aluminum Hydride

BY R. T. GILSDORF AND F. F. NORD

Because of the structural similarity existing between amidines and amides, interest in the former class of compounds was fostered in these laboratories[1a,b] when reports[2,3] appeared in the literature on the reduction of amides with lithium aluminum hydride. An investigation was undertaken to ascertain whether amidines would behave analogously to amides when similarly treated. Study of the literature revealed that, in general, amidines in the free state are quite prone to hydrolysis to the corresponding amides, thus rendering them unsuitable for comparison with amides since the products could not be established as arising from the reduction of the amidine or the amide generated from the amidine by hydrolysis.

However, one class of amidines, *i.e.*, those which are N,N-disubstituted aromatic derivatives, seem

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