with trichlorosilane to produce isomeric intermediates which in turn were used to produce isomeric end products. These end products contain small quantities of bis- bodies, which because of their extremely high boiling points, could not be separated from the parent material. In general, materials containing the following bonds showed a decreasing order of thermal stability: $C_6H_5C_6H_4Si > C_6H_5Si > C_6H_5OSi > C_6H_5OC_6H_4Si > C_6H_5C_6H_4OSi > C_6H_{11}C_6H_4Si > C_6H_5C_6H_4C_6H_4Si > C_nH_{2n+1}C_6H_4Si$.

ACKNOWLEDGMENT

The author is grateful to G.M. Rapp, who directed the heat transfer fluid program, and to the trustees of the John B. Pierce Foundation for their support of this project as an internal program.

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RECEIVED for review October 30, 1961. Accepted April 26, 1962.

Organo-Silicon Nitrogen Compounds

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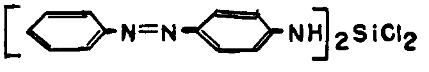
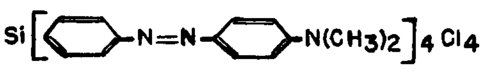
FORMATION of tetraanilinosilane by the reaction of aniline in benzene with tetrachlorosilane was reported by Reynolds (*7*). This reaction had been investigated earlier by Harden (*4*), who reported the production of one equivalent of dianilinodichlorosilane and two of aniline hydrochloride. Two silicon nitrogen-bonded compounds, dichlorodi(*p*-aminoazobenzene)silane,



and tetra(N,N-dimethylaminoazobenzene)silane tetrachloride,



have now been prepared by this method from *p*-aminoazobenzene and N,N-dimethylaminoazobenzene, respectively, in 74.4 to 78.5% yields (Table I). Both were formed as dark red crystals.

The infrared spectra of these compounds were determined between 3 and 15 microns (Figures 1 and 2).

In preparation of dichlorodi(*p*-aminoazobenzene)silane, *p*-aminoazobenzene hydrochloride was another product, identified by its infrared spectrum (Figure 3) which was determined between 3 and 15 microns.

The fact that tetrachlorosilane did not react with azobenzene indicated that only the amino group was affected in the reactions of the aminoazobenzenes with tetrachlorosilane.

Waterman (*8*) prepared a series of silicon-nitrogen compounds, namely, trichlorodiethylaminosilane, dichlorobis(diethylamino)silane, chlorotri(diethylamino)silane, and tetra(diethylamino)silane, and obtained their infrared spectra. A comparison of all these spectra with the spectrum of diethylamine indicates that the new bands occur between 7.45 and 7.48, 9.38 and 9.41, 9.69 and 9.78, 10.66 and 10.8, and 12.6 and 12.68 microns, and may be due to Si—N bonding. Strong new bands were obtained at 9.2, 9.7, and 12.4 microns for dichlorodi(*p*-aminoazobenzene)silane and at 9.35 microns for tetra(N,N-dimethylaminoazobenzene)silane tetrachloride. Weak peaks occur in the latter compound at 9.7 and 12.4 microns.

Since new absorption bands occur in all these spectra at 9.2 to 9.4, 9.69 to 9.71, and 12.4 microns it seems likely that they are due to Si—N bonding.

Table I. Analysis of Si—N Bonded Compounds

Compound	Yield, %	Silicon, %		Nitrogen, %		Chlorine, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
$[C_6H_5—N=N—C_6H_4—NH]_2SiCl$	74.4	5.68	5.56	17.06	17.01	14.62	14.02
$Si[C_6H_5—N=N—C_6H_4—N(CH_3)_2]Cl_4$	78.5	2.61	2.56	15.6	15.1	13.3	13.07

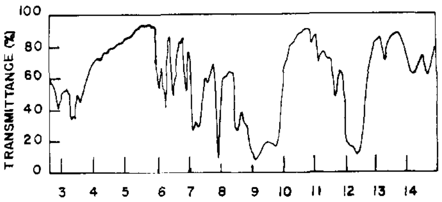


Figure 1. Infrared spectrum for dichlorodi(*p*-aminoazobenzene)silane

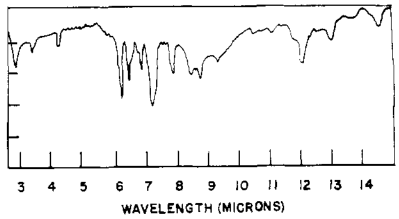


Figure 2. Infrared spectrum for tetra(N,N-dimethylaminoazobenzene)silane tetrachloride

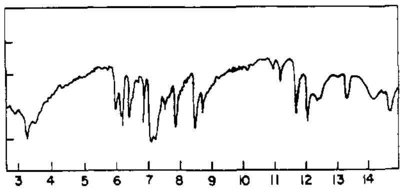


Figure 3. Infrared spectrum for *p*-aminoazobenzene hydrochloride

EXPERIMENTAL

The method and apparatus used in preparing the Si—N bonded compounds were similar to those used by Lanning and Moore (*6*) to prepare acyloxysilanes. The tetrachlorosilane was purified by distillation. *p*-Aminoazobenzene and N,N-dimethylaminoazobenzene were dried at 110° C. Anhydrous benzene was used as a solvent.

To prepare dichlorodi(*p*-aminoazobenzene)silane, 10 grams of tetrachlorosilane dissolved in 50 ml. of anhydrous benzene was added dropwise to a slurry of 47 grams of *p*-aminoazobenzene dispersed in 200 ml. of benzene. The temperature was kept at 0°, and the tetrachlorosilane added slowly over 1.5-hour period. The mixture was stirred during the addition and for 2.5 hours afterward. A red-violet substance, *p*-aminoazobenzene hydrochloride, separated and was removed by filtering with a Selas crucible. The solid gave an infrared spectrum identical to that of a known sample of pure *p*-aminoazobenzene hydrochloride.

The dichlorodi(*p*-aminoazobenzene)silane was separated from the filtrate by adsorption chromatography on a 15-inch column. A one to one mixture of silicic acid (Mallinckrodt analytical reagent grade, 100 mesh) and Supercel (*1*) was a good adsorbent. Three ml. of the filtrate was poured into the top of the column after it had been moistened with benzene. When benzene was added as the eluting agent, different bands were obtained. By further eluting with benzene and carbon disulfide, unreacted *p*-aminobenzene was removed. Elution with acetone removed the product from the adsorption column.

From this the red powder obtained by evaporating the filtrate could be easily separated. Washing first with carbon disulfide and then with benzene removed all the unreacted *p*-aminoazobenzene and left a good solid product. The analysis is given in Table I.

Tetra(N,N-dimethylaminoazobenzene)silane tetrachloride was made by the method used for dichlorodi(*p*-aminoazobenzene)silane. The tetrachlorsilane solution was added slowly to a slurry of N,N-dimethylaminoazobenzene at −12°. The reaction mixture was stirred for 4 hours, and the red precipitate that formed was filtered and dried at 90° C. Results of analyses are given in Table I. Rapid reaction with $AgNO_3$ indicated that the chlorine was in ionic form.

Nitrogen was determined by the Kjeldahl (*3*) method. In the case of tetra(N,N-dimethylaminoazobenzene)silane tetrachloride the micro-Kjeldahl method was used.

Silicon was determined by the method of Hyde and Delong (*5*). Best results were obtained by using fuming nitric acid. Chlorine was determined by the Carius (*2*) method.

The infrared spectra were obtained with a Perkin-Elmer, Model 137, infrared spectrometer. The compounds tested were made into pellets with potassium bromide: 1 mg. of compound was mixed with 500 mg. of potassium bromide.

ACKNOWLEDGMENT

This work was supported by National Institutes of Health Grant No. RG-6881.

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RECEIVED for review May 21, 1962. Accepted July 2, 1962. From the M.S. thesis of V.K. Emmanuel.