

tion of benzyl cyanide in the presence of sodamide¹ and (2) the conversion of β -methyl- β -phenylglycidate through the aldehyde and oxime² are either long or subject to difficulties, an attempt was made to convert α -chloroethylbenzene into the desired nitrile.

Our first attempt was to treat α -chloroethylbenzene with an alcoholic solution of sodium cyanide by the procedure used in preparing benzyl cyanide from benzyl chloride.³ Instead of the expected nitrile, there was obtained only ethyl (α -phenylethyl) ether,⁴ b. p. 67° (11 mm.); micro b. p. 183° (745 mm.) with decomposition; n_D^{20} 1.4848; d_4^{20} 0.9212.

Inasmuch as the ether was formed in preference to the nitrile, it appeared desirable to carry out the reaction in the absence of alcohol. Consequently α -chloroethylbenzene was heated with cuprous cyanide in the manner of the von Braun nitrile synthesis. Runs were made with and without potassium iodide⁵ and copper sulfate⁶ as catalysts. When the reaction mixture was heated in an oil-bath at 130°, a vigorous reaction set in, accompanied by the evolution of hydrogen cyanide. It was found best to chill the reaction flask after fifteen minutes and to extract the reaction mixture with benzene. A colorless oil distilled at 134–135° (ca. 1 mm.), micro b. p. 311° (737 mm.); n_D^{20} 1.5939; d_4^{20} 0.9968. This product contained neither nitrogen nor chlorine, but decolorized bromine in cold carbon tetrachloride. These physical⁷ and chemical properties approximate those of the diphenylbutenes (distyrenes).

The position of unsaturation was determined by treating the liquid with a solution of hydrogen peroxide in *t*-butyl alcohol in the presence of osmium tetroxide.⁸ After removal of the solvent under diminished pressure, benzaldehyde distilled. No other homogeneous fraction was isolated. The benzaldehyde was characterized as the 2,4-dinitrophenylhydrazone.

Benzaldehyde should be obtained by the cleavage of either 1,3-diphenyl-1-butene (I) or 1,3-diphenyl-2-methyl-1-propene (II). The latter should also yield methyl benzyl ketone, whereas the hydratropaldehyde of the former might be easily oxidized further. Failure to isolate a second degradation product from the hydroxylation mixture indicated I as the more probable structure of our compound.

A liquid distyrene of formula I has been described by numerous investigators. From it

(1) Baldinger and Nieuwland, *THIS JOURNAL*, **55**, 2851 (1933); Crawford, *ibid.*, **56**, 140 (1934).

(2) Newman and Closson, *ibid.*, **66**, 1553 (1944).

(3) "Organic Syntheses," Col. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 107.

(4) Schramm, *Ber.*, **26**, 1710 (1893).

(5) "Organic Syntheses," Vol. XXIV, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 97.

(6) Koelsch and Whitney, *J. Org. Chem.*, **6**, 795 (1941).

(7) Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Corporation, New York, N. Y., 1946, p. 398.

(8) Milas and Sussman, *THIS JOURNAL*, **58**, 1302 (1936).

Stobbe and Posnjak⁹ obtained a dibromide melting at 102°. This product is described by Stoermer and Kootz¹⁰ and Marion¹¹ as a mixture of racemic dibromides which are derived from the *cis* form of I. The *trans* isomer of I is a solid melting at 47°.¹¹

Bromination of our liquid hydrocarbon by the procedure of Stobbe and Posnjak⁹ gave a white crystalline compound melting at 102°. When this was mixed with an authentic sample of the dibromo derivative of *cis*-1,3-diphenyl-1-butene obtained from cinnamic acid by the method of Stoermer and Kootz,¹⁰ no melting point depression was observed. Our hydrocarbon is thus shown to be *cis*-1,3-diphenyl-1-butene.

Experimental

α -Chloroethylbenzene was prepared by a modification of the procedure of Kharasch and Kleiman.¹² Five hundred twenty grams (5 moles) of styrene containing its inhibitor was placed in a 1-liter three-necked flask equipped with a mercury-sealed stirrer, an inlet tube and an exit tube immersed in a reservoir of mercury. The flask was immersed in an ice-salt-bath and dry hydrogen chloride gas was passed in under a pressure of 50 to 75 mm. Saturation of the styrene with hydrogen chloride required eight to twelve hours. Distillation of the reaction mixture under diminished pressure gave α -chloroethylbenzene in yields of 80–90%.

Preparation of 1,3-Diphenyl-1-butene (I).—This preparation was carried out in a hood. One hundred seventy-five grams (1.25 moles) of α -chloroethylbenzene was added to 112 g. of commercial cuprous cyanide (dried and undried material gave identical results) in a 500-ml., three-necked flask equipped with an effective mercury-sealed stirrer, a thermometer and an uncooled reflux condenser. A glass tube connected the top of the condenser to a coil and receiver packed in an ice-salt-bath. The reaction flask was heated in an oil-bath. At a temperature of 130° a vigorous evolution of hydrogen cyanide occurred. After 40 to 45 ml. of hydrogen cyanide was condensed in the coil and receiver, the temperature in the flask rose suddenly and the reaction proceeded more vigorously. The condenser was now flooded with water. After ten minutes, the oil-bath was replaced by a cold water-bath. The cold reaction mixture was extracted with four 100-ml. portions of benzene.

The benzene was removed and the crude product fractionated under reduced pressure through a one-foot column packed with glass helices. A colorless oil, distilling at 134–135° (ca. 1 mm.), was obtained; yield, 41%.

(9) Stobbe and Posnjak, *Ann.*, **371**, 287 (1909).

(10) Stoermer and Kootz, *Ber.*, **61**, 2330 (1928).

(11) Marion, *Can. J. Research*, **16B**, 213 (1938).

(12) Kharasch and Kleiman, *THIS JOURNAL*, **65**, 11 (1943).

KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN

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Complete Chlorination of Methyltrichlorosilane¹

BY PHILIP A. DI GIORGIO,² LEO H. SOMMER AND FRANK C. WHITMORE

Prior publications^{3,4} on the synthesis and properties of chloromethyl silicon compounds have

(1) Paper XX in a series on organosilicon compounds. For paper XIX see *THIS JOURNAL*, **70**, 2876 (1948).

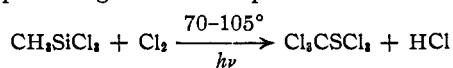
(2) Present address: Research Laboratory, General Electric Co., Schenectady, N. Y.

(3) (a) Krieble and Elliott, *ibid.*, **67**, 1810 (1945); (b) Krieble and Elliott, *ibid.*, **68**, 2291 (1946).

(4) Whitmore and Sommer, *ibid.*, **68**, 481 (1946).

included none derived from methyltrichlorosilane. We have synthesized trichloromethyltrichlorosilane, $\text{Cl}_3\text{CSiCl}_3$, and have studied the hydrolysis of this compound.⁵

Trichloromethyltrichlorosilane is a white, waxy solid melting at 115–116° and boiling at 155–156° at atmospheric pressure. It is readily obtained in better than 55% yield by the photochemical chlorination of methyltrichlorosilane at 70–150°. The per-halogenated compound is sensitive to

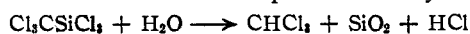


moisture and is readily soluble in a wide variety of organic solvents.

It is interesting to compare the liquid range of trichloromethyltrichlorosilane with those of its carbon and silicon analogs. The following table shows how the liquid range of symmetrical compounds, *i. e.*, the difference between the melting point and boiling point at atmospheric pressure, is affected by substitution of silicon for carbon.

Compound	Approximate liquid range, °C.
Cl_3CCl_3	0
$\text{Cl}_3\text{CSiCl}_3$	40
$\text{Cl}_3\text{SiSiCl}_3$	145
$(\text{CH}_3)_3\text{CC}(\text{CH}_3)_3$	3
$(\text{CH}_3)_3\text{CSi}(\text{CH}_3)_3$	30
$(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$	100

In marked contrast to mono- and dichloromethylchlorosilanes which require alkaline reagents for cleavage of the Si–C bond, trichloromethyltrichlorosilane readily undergoes fission of the Si–C linkage simply upon treatment with distilled water at room temperature. Hydrolysis



with cold concentrated hydrochloric acid and with cold concentrated ammonium hydroxide both also give fission of the silicon–carbon linkage with formation of chloroform.

Lower chlorination products of methyltrichlorosilane appear less susceptible than trichloromethyltrichlorosilane to hydrolytic cleavage of the silicon–carbon bond. When a mixture of lower-boiling compounds from the synthesis of the perchloro compound was hydrolyzed on cracked ice, there was obtained after drying a white powder containing 20% chlorine bound to carbon.

Experimental

Preparation of Methyltrichlorosilane.—This compound was prepared in 55% yield by the reaction of magnesium bromide with silicon tetrachloride.⁶ The product boiled at 64.5 to 64.8° at 730–735 mm.

(5) Reference 3a mentioned incidentally, as a private communication from Dr. W. F. Gilliam, the isolation of trichloromethyltrichlorosilane and its reaction with water to give chloroform, silica and hydrochloric acid. Dr. Gilliam tells us that he obtained his trichloromethyltrichlorosilane from the vapor phase chlorination of dimethyldichlorosilane at elevated temperature in the presence of copper gauze.

(6) Gilliam, Liebhaufsky and Winslow, *THIS JOURNAL*, **63**, 801 (1941).

Anal. Calcd. for $\text{CH}_3\text{Cl}_3\text{Si}$: equivalent weight, 49.8; Cl, 71.2. Found on separate successive fractions: equivalent weight, 49.7, 49.9, 49.7, 49.6, 49.7; Cl, 70.9, 71.0, 70.9, 71.1, 71.0.

Synthesis of Trichloromethyltrichlorosilane.—In a 25 × 4.6-cm. test-tube was placed 130 g., 0.87 mole, of methyltrichlorosilane. The reaction vessel was equipped with an alkali-boiled rubber stopper carrying a 20-cm. brine-cooled worm-type condenser and a thermometer and coarse fritted-glass inlet tube both extending below the surface of the liquid in the reactor. The condenser was open to the atmosphere through a Dry Ice and acetone trap.

The methyltrichlorosilane was illuminated with a General Electric Co. "Sunlight Lamp," style BM6, of 450 watts equipped with a type S-1 "Mazda" bulb situated about 1.5 feet from the reaction vessel. During the course of the chlorination the reaction mixture was kept at gentle reflux by heat from a bunsen burner. Commercial chlorine from a cylinder was then run in after passage through two concentrated sulfuric acid scrubbers. Hydrogen chloride was emitted steadily from the cold trap during the course of the chlorination.

After two and one-half hours, the reaction temperature had risen to 150°, and the reaction was shut down due to clogging of the condenser with a solid. Rapid evolution of hydrogen chloride was still proceeding at this point. When the liquid reaction mixture was allowed to cool, solidification started at 120° and was complete at 105°. The cold trap contained a yellow liquid, 60 g. of which volatilized at room temperature and 10 g. of which did not volatilize.

The 170 g. of white, waxy, crude product was distilled at 740 mm. through a six-inch column packed with $3/32$ -inch glass helices and connected to a condenser maintained at 120° to prevent plugging by solidification. The distillate was collected in a long test-tube cooled in an ice-bath.

After an 18-g. fore-run, there was collected a 121 g. main fraction boiling at 155–156°. Further distillation of the 30-g. residue gave vigorous decomposition. The main fraction, 0.48 mole, constituted a 55% yield of trichloromethyltrichlorosilane. Losses incurred by gas entrainment and decomposition probably accounted to a great extent for the lowered yield.

Anal. Calcd. for CCl_3Si : Cl, 84.2. Found: Cl, 83.7, 83.1.

Trichloromethyltrichlorosilane melted at 115–116° both in a sealed capillary and on the surface of a pool of mercury in a test-tube blanketed with dry air. In an ordinary open capillary the melting point was 114–116°. Trichloromethyltrichlorosilane dissolved readily in pentane, benzene, chloroform, carbon tetrachloride, liquid methyl bromide, ethyl ether, *n*-butyl ether, dioxane and 2-nitropropane.

Hydrolysis of Trichloromethyltrichlorosilane. A. With Water.—An ethereal solution of trichloromethyltrichlorosilane was hydrolyzed by pouring into iced water and allowing to stand for ten hours at room temperature. Fractionation of the dried ether layer gave a material identified as chloroform, b. p. 57–59° at 730 mm., n_D^{20} 1.436–45, which gave a positive carbylamine test. Evaporation of the water layer gave a powdery white solid free of halogen (Volhard titration following Parr bomb fusion) and so presumed to be silica.

When a mixture of lower boiling fractions from the synthesis of the trichloromethyl compound was hydrolyzed on ice, there was obtained after evaporation and drying for twelve hours at 130° a white powder containing 20% chlorine bound to carbon.

B. With Hydrochloric Acid.—A solution of 6.3 g. of trichloromethyltrichlorosilane in 20 ml. of anhydrous ether was added to a mixture of 20 g. of ice and 20 ml. of concentrated hydrochloric acid. After ten minutes shaking, the layers were separated and evaporated; the resulting residues weighed 1.7 g. Since the theoretical weight of silica was 1.5 g., it was concluded that little or no halogenated polyorganosiloxane was formed.

C. With Ammonium Hydroxide.—Addition of 67 ml. of a butyl ether solution of 30 g. of trichloromethyltrichlorosilane to 50 ml. of concentrated ammonium hydroxide in the cold gave a curdy, white precipitate. This material was filtered, washed with butyl ether, dried, washed with 5% aqueous ammonia to remove ammonium chloride, and finally dried at 130° for three hours. The resulting 6.3 g. of tan powder was free of bound halogen and gave 80% residue on ashing; thus it was apparently partially hydrated silica.

From the butyl ether layer and washings was isolated 11 g. of material b. p. 56–58° at 730 mm., n_D^{20} 1.444. This product was heavier than water, gave a positive Beilstein test, was inert to hot 95% ethanolic silver nitrate, and had a chloroform odor.

Anal. Calcd. for CHCl_3 : Cl, 89.1. Found: Cl, 87.5.

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THE SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
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The Photodecomposition of Nitrobenzene

BY S. H. HASTINGS^{1a} AND F. A. MATSEN

Nitrobenzene exhibits in the vapor phase a strong continuous absorption in the 2600 Å. region¹ in contrast to most other monosubstituted benzenes which yield discrete spectra in the same region. On the long wave length shoulder of the nitrobenzene continuum are four relatively weak bands. In Fig. 1 is a microphotometer tracing of the vapor spectrum of nitrobenzene. The occur-

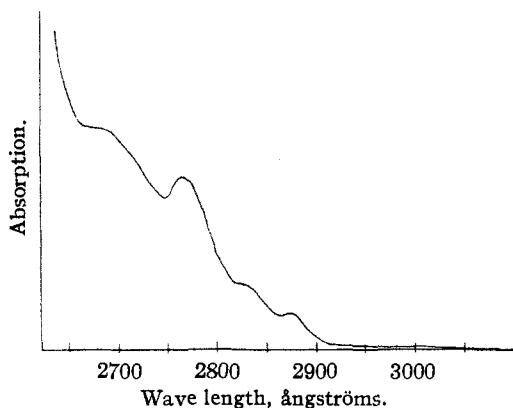


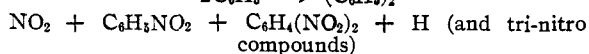
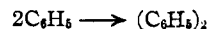
Fig. 1.—Microphotometer tracing of near ultraviolet absorption spectrogram of nitrobenzene vapor.

rence of the continuum suggests that photodecomposition takes place, evidence for which was obtained by Shelegova¹ in the form of a yellow tarnish on the walls of the reaction chamber. The following reactions were postulated by Shelegova.



(1a) Humble Oil and Refining Company Fellow.

(1) O. N. Shelegova, *J. Exp. Theoret. Phys. U. S. S. R.*, IX, 1527 (1939).



No evidence was offered for the formation of nitrogen dioxide or polynitrated benzenes.

The suggestion that the aromatic nitro compounds split off oxygen in the photodecomposition process frequently has been made. Aniline and nitrobenzene in the liquid state when irradiated produce *p*-aminophenol and other products some of which require the formation of nitrosobenzene as an intermediate.² *o*-Nitrobenzaldehyde forms *o*-nitrosobenzoic acid.³ The NO_2 molecule itself is known to decompose into nitric oxide and atomic oxygen.⁴ It seemed worthwhile in view of these facts to reinvestigate the photodecomposition of nitrobenzene in the vapor phase.

Nitrobenzene with nitrogen as a carrier was passed through a quartz cell irradiated by two 220 v. d.c. arcs with brass negative electrodes^{4a} and iron positive electrodes. The exhaust vapor

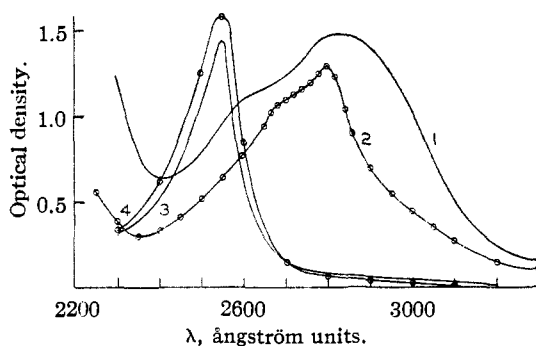


Fig. 2.—Ultraviolet spectra in cyclohexane solution of: 1, unknown cyclohexane-soluble product; 2, nitrosobenzene; 3, oxidation product of 1; 4, nitrobenzene.

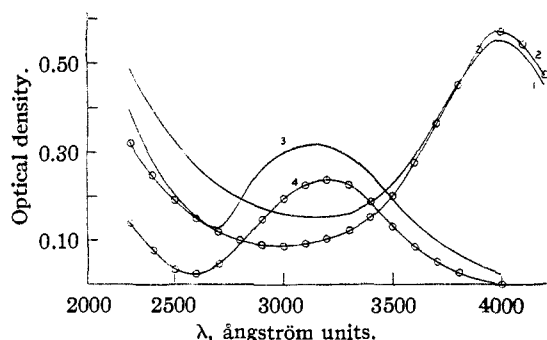


Fig. 3.—Ultraviolet spectra of: 1, 1 N NaOH solution of base-soluble product; 2, 1 N NaOH solution of *p*-nitrophenol; 3, 4.5 N HCl solution of base-soluble product; 4, 4.5 N HCl solution of *p*-nitrophenol.

(2) L. Vecchiotti and C. Piccinini, *Gazz. chim. ital.*, **61**, 626 (1931).

(3) (a) F. Weigert and L. Kummerer, *Ber.*, **46**, 1207 (1913);

(b) P. A. Leighton and F. A. Lucy, *J. Chem. Phys.*, **2**, 756, 760 (1934).

(4) R. G. Dickinson and W. P. Baxter, *THIS JOURNAL*, **50**, 774 (1928).

(4a) Zinc and copper emit strongly in the wave length region of the nitrobenzene continuum.