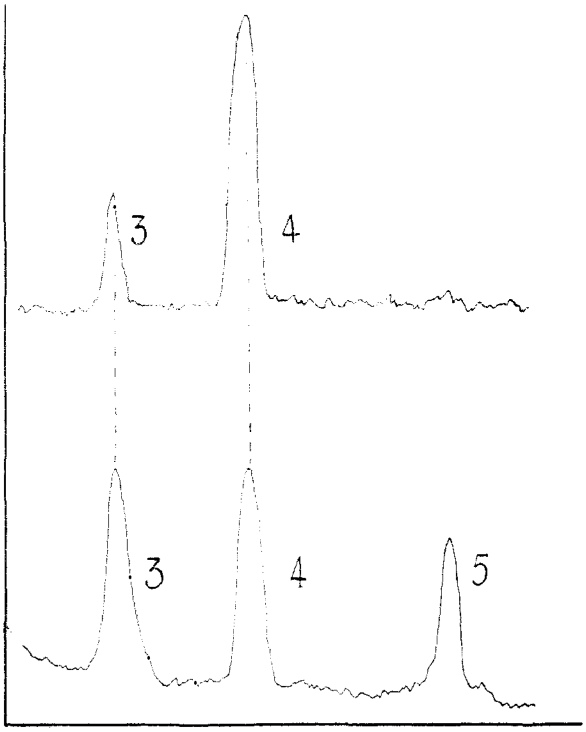


Fig. 2.—Raman spectra for silicon chloroiodides: (A) upper, $SiCl_3I$ at 325°; (B) lower, $SiCl_3I$ at 400°.

Raman spectrum for the liquid obtained by treating silicon trichloroiodide with hydrogen iodide at 325°. The first chlorine is the most difficult to replace.

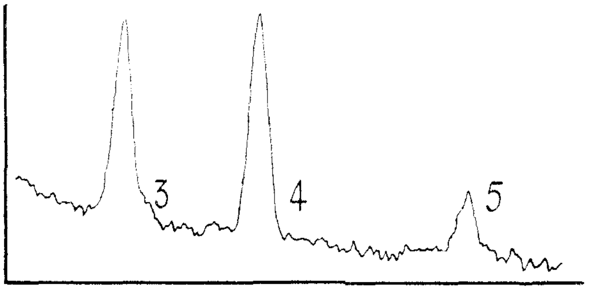


Fig. 3.—Raman spectrum for silicon chloroiodides: $SiCl_3I$ + HI at 325°.

Chloroiodides of tin were described early in the literature but were later disproved (Lenormand,[11] Auger,[12] Räder[13]). There is no record in the literature of the chloroiodides of germanium. However germanium and tin chloroiodides exist but cannot be isolated. They can be prepared by either causing germanium tetrachloride or stannic chloride to react with hydrogen iodide or by mixing the halides ACl_4 and AI_4 either in the pure form or in a solvent such as carbon disulfide. The reaction, which takes place when ACl_4 and ABr_4 are mixed, is more rapid for tin than for germanium.[14] For the same element (germanium or tin) the chlorine–bromine exchange reaction proceeds faster than does the chlorine–iodine exchange reaction. The study of Raman spectra for these mixtures or solutions definitely shows, as in the case of the chlorobromides of Ge and Sn, the existence of new molecules. Tables IV and V show the ν_1 frequencies of the three chloroiodides of germanium and tin and similar frequencies for the chlorobromides. The pattern of the lines is unchanged when we replace chlorine by iodine, instead of chlorine by bromine. There is also great similarity between the spectra for the germanium and tin compounds.

TABLE IV

ν_1 frequencies, cm.$^{-1}$

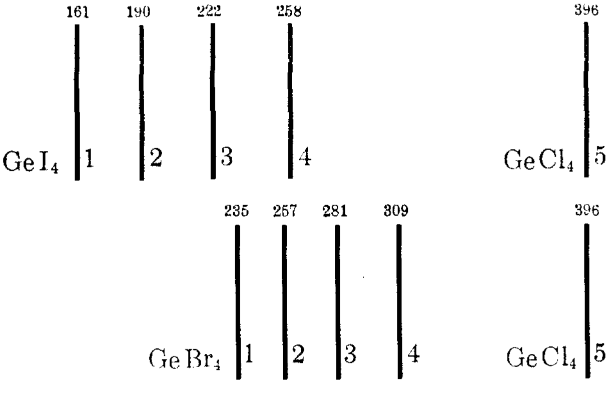
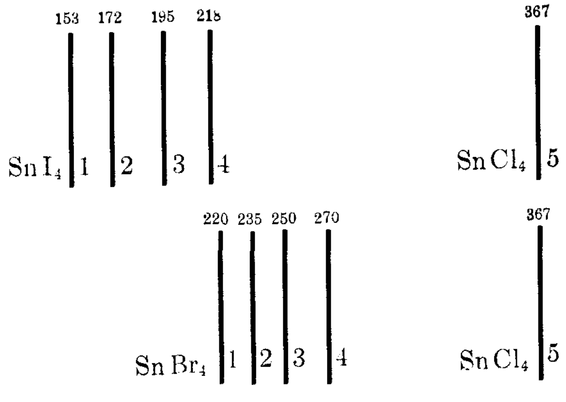


TABLE V

ν_1 frequencies, cm.$^{-1}$



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[11] M. C. Lenormand, *J. pharm. chim.*, **8**, 249 (1898).

[12] V. Auger, *Compt. rend.*, **149**, 860 (1909).

[13] M. G. Räder, *Z. anorg. Chem.*, **130**, 325 (1923).

[14] M. L. Delwaulle, *Compt. rend.*, **232**, 54 (1951).

Methylsulfur Trichloride and Analogous Compounds[1,2]

BY IRWIN B. DOUGLASS, KAY ROBERT BROWER AND FREDERIC T. MARTIN

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In a recent paper from this Laboratory the preparation and reactions of methylsulfur trichloride were reported.[3] The reaction between methyl disulfide and chlorine was described as

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[1] This paper describes work done on Project NR-055-165 under Contract Nonr-647(00) with the Office of Naval Research, United States Navy.

[2] Taken in part from the Master's Thesis of Kay Robert Brower.

[3] K. R. Brower and I. B. Douglass, THIS JOURNAL, **73**, 5787 (1951).

$$(CH_3S)_2 \xrightarrow[-20^\circ]{Cl_2} CH_3SCl \xrightarrow[-20^\circ]{Cl_2} CH_3SCl_3 \xrightarrow[30^\circ]{\text{decomp.}} ClCH_2SCl + HCl \quad (1)$$

There appeared almost simultaneously in Germany a paper[4] in which it was stated that methyl disulfide reacts with chlorine to form a solid, $C_2H_6Cl_2S_2$, as previously described by Rieche.[5]

All efforts in this Laboratory to obtain a solid of the composition $C_2H_6S_2Cl_2$ have been fruitless. Even in liquid butane at the temperature of solid carbon dioxide chlorine seems to split the S–S bond of methyl disulfide to give a highly colored solution of methanesulfenyl chloride. There is no more than momentary evidence of solid formation until one molecular equivalent of chlorine has been absorbed after which further addition of chlorine causes the precipitation of methylsulfur trichloride.

The reaction between disulfides and chlorine, or more correctly between sulfenyl chlorides and chlorine, to form sulfur trichlorides is capable of wide application. The reaction has been extended and ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, *n*-pentyl-, chloromethyl- and phenylsulfur trichlorides have been prepared. No precipitate was obtained when *t*-butyl disulfide was chlorinated under the same conditions. Dichloromethanesulfenyl chloride reacted with liquid chlorine to form a precipitate which, however, decomposed at such a low temperature that it could not be isolated. Trichloromethanesulfenyl chloride and chlorine give no evidence of reaction. Benzyl disulfide was desulfurized to benzyl chloride.

The simple alkylsulfur trichlorides decompose chiefly according to the reaction

$$RCH_2SCl_3 \longrightarrow HCl + RCHClSCl \quad (2)$$

On the other hand, chloromethyl- and phenylsulfur trichlorides decompose, at least in part, according to the equation

$$RSCl_3 \longrightarrow RSCl + Cl_2 \quad (3)$$

There is some evidence that both reactions may occur simultaneously.

Just as methylsulfur trichloride reacts readily with water so also ethylsulfur trichloride hydrolyzes to form ethanesulfinic acid, $C_2H_5SO_2H$.

Experimental

In most of the experiments described in this study the following procedure was employed: The reaction was carried out in a large test-tube partially immersed in a bath of acetone and solid carbon dioxide using liquid butane (C.P. grade) as the solvent.[6] Three to five ml. of the disulfide was added to the cold solvent and a gentle stream of chlorine was led into the space above the solution. Chlorination was discontinued when the color of the sulfenyl chloride first formed was no longer visible in the thick slurry of white crystals. After centrifuging, the mother liquor was decanted, the solid was washed twice with additional butane and was quickly transferred as a slurry to a modified Skau filtration tube[7] and centrifuged.

The tube containing the moist solid was then evacuated for 30–40 minutes at −20 to −40° until the solid had become a free-flowing powder.

For analysis, samples of the dry solids were sealed in strong glass bulbs and introduced unopened into Parr bombs. The compounds were prevented from decomposing during the sealing operation by keeping the bulbs buried in powdered solid carbon dioxide.

Decomposition temperatures were determined in melting point tubes by allowing the bath to warm up at the rate of about 1° per minute. These temperatures, which marked the sudden transition from white solid to yellow liquid with evolution of gas, merely represent relative degrees of stability and are not reliable as constants for use in identification.

The difficulty of working with these unstable compounds led to analytical results with an unusually wide margin of error. The method of formation and chlorine content found, however, leave little doubt as to the identity of the compounds. The high chlorine content of isopropylsulfur trichloride suggests that there was some chlorine substitution in the isopropyl group.

COMPOUNDS PREPARED

Compound	Temperature of decomposition, °C.	Analyses, % Calcd. Cl	Analyses, % Found Cl
CH_3SCl_3[3]	30		
$C_2H_5SCl_3$	11–13	63.51	61.7, 61.3
n-$C_3H_7SCl_3$	9	58.60	57.5
Iso-$C_3H_7SCl_3$	Below 9	58.60	63.1, 61.5
n-$C_4H_9SCl_3$	5–10	54.40	52.8, 53.7
n-$C_5H_{11}SCl_3$	5–8	50.76	50.7; 50.8
$ClCH_2SCl_3$	20–25	75.53	69.5
$C_6H_5SCl_3$	Below 10	40.5	40.6

Decomposition of Sulfur Trichlorides.—When methylsulfur trichloride (90 g.) was allowed to decompose in an evacuated system the decomposition gases carried over into a cold-trap approximately 3 g. of reddish liquid and an equal weight of white solid. The latter was identified as methylsulfur trichloride by hydrolysis to sodium methanesulfinate and transformation to methyl benzyl sulfone. This result indicates either that methylsulfur trichloride is volatile without decomposition or that some decomposition according to equation (3) took place with recombination occurring in the cold-trap.

Ethylsulfur trichloride (approx. 50 g. obtained from 42 g. of C_2H_5SH) was allowed to decompose and the liquid product was distilled, yielding 26 g. of product having b.p. 38–42° (28 mm.), $n^{20}D$ 1.5100 and d^{20}_4 1.339. These properties identify the compound as 1-chloromethanesulfenyl chloride.[8] The identification was confirmed by aqueous chlorination to 1-chloroethanesulfonyl chloride which was identified as the *p*-toluidide, $CH_3CHClSO_2NHC_6H_4CH_3$-*p*, m.p. 85°. The melting point was not lowered when the compound was mixed with a sample prepared from the sulfonyl chloride resulting from the aqueous chlorination of trithioacetaldehyde.[9] The *p*-toluidide was analyzed.

Anal. Calcd. for $C_9H_{12}ClO_2NS$: C, 46.25; H, 5.18. N, 5.99. Found: C, 46.3; H, 5.2; N, 6.2.

Chloromethylsulfur trichloride decomposed with the evolution of a small amount of hydrogen chloride, indicating some decomposition according to equation (2). The vapors also liberated iodine from moist potassium iodide–starch paper, suggesting the evolution of free chlorine according to equation (3). The yellow liquid product of the decomposition consisted chiefly of chloromethanesulfenyl chloride as was proven by aqueous chlorination to the corresponding sulfonyl chloride and formation of its *p*-toluidide, $ClCH_2SO_2NHC_6H_4CH_3$-*p*.[10]

Phenylsulfur trichloride appears to decompose reversibly so readily that the solid cannot be washed free of color. In attempting to evaporate the residual butane from phenylsulfur trichloride, decomposition also took place to some extent and the final product was yellow in color.

Ten grams of the phenylsulfur trichloride, moist with isopentane, was allowed to decompose and gave off a gas, presumably chlorine, which readily liberated iodine from a po-

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(4) E. Schneider, *Chem. Ber.*, **84**, 911 (1951).

(5) Rieche, *Ann.*, **92**, 356 (1854).

(6) The higher homologs of methylsulfur trichloride are soluble in methylene chloride which was originally recommended as a reaction solvent.[3]

(7) E. L. Skau, *J. Phys. Chem.*, **33**, 951 (1930).

(8) I. B. Douglass and F. T. Martin, *J. Org. Chem.*, **15**, 795 (1950).

(9) E. Müller and H. Raudenbusch, *Ber.*, **64**, 94 (1931).

(10) T. B. Johnson and I. B. Douglass, THIS JOURNAL, **63**, 1571 (1941).

tassium iodide solution. The orange-red, liquid product of the decomposition was purified by distillation. One fraction, amounting to a yield of about 20%, had b.p. 80° (17 mm.), $n^{20}\text{D}$ 1.610 and d^{20}_4 1.23. These properties when compared with those previously reported[8] identify the compound as benzenesulfenyl chloride.

Hydrolysis of Sulfur Trichlorides.—When added to a cold sodium bicarbonate solution ethylsulfur trichloride formed sodium ethanesulfinate which reacted on boiling with benzyl chloride to form benzyl ethyl sulfone. The latter melted at 84° and the melting point was unchanged when the sample was mixed with benzyl ethyl sulfone prepared by the oxidation of benzyl ethyl sulfide.

Unsuccessful Attempts to Prepare Sulfur Trichlorides.—Benzyl disulfide (5 g.) was chlorinated at −40°, but no precipitate formed. The reaction mixture was distilled under reduced pressure and there was obtained 2 g. of liquid with the properties: b.p. 89° (37 mm.), $n^{20}\text{D}$ 1.540, d^{20}_4 1.11, which identify the product as benzyl chloride.

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The Structure of Isoamidone. I

BY NELSON R. EASTON, SAMUEL J. NELSON[1] AND VELMER B. FISH

RECEIVED APRIL 29, 1952

While carrying out some work on 4,4-diphenyl-6-dimethylamino-3-hexanone we had occasion to prepare several derivatives. The melting points of these compounds agreed very closely with those reported[2] for Isoamidone I, and the melting points of the hydrochloride of this substance, when taken in the same melting point apparatus was the same as that of the hydrochloride of 4,4-diphenyl-6-dimethylamino-3-hexanone. No depression in melting points was observed on mixing.

These data prove that Isoamidone I is 4,4-diphenyl-6-dimethylamino-3-hexanone. A logical explanation for the finding of this compound in the mother liquors from the synthesis of Amidone is that the propylene chlorohydrin, which was used in the preparation of the dimethylaminochloropropane, was contaminated with ethylene chlorohydrin.

Experimental

The 6-dimethylamino-4,4-diphenyl-3-hexanone was prepared by the procedure[3] of Dupre, *et al.*, in which 4-bromo-2,2-diphenylbutanenitrile is aminated with dimethylamine and then the ketone is prepared by the usual Grignard reaction. The ketone was usually isolated as the hydrobromide and then converted to the desired derivative.

Preparation of Derivatives of 6-Dimethylamino-4,4-diphenyl-3-hexanone.—The hydrobromide was dissolved in warm water and the solution was made basic with sodium hydroxide. The oil was extracted with ether and the ether was dried over magnesium sulfate and the solvent distilled. Concentrated hydrochloric acid and ethanol were added. The mixture was concentrated to dryness and crystallized on scratching. It was recrystallized from acetone and melted at 173.5–175°,[4] not depressed on an admixture of Isoamidone I hydrochloride of m.p. 173.5–175°.

Anal. Calcd. for $C_{20}H_{26}NOCl$: Cl, 10.68. Found: Cl, 10.92.

Methiodide (from absolute ethanol), m.p. 199.5–200.5°; reported for Isoamidone I methiodide[2] 195–196°.

Anal. Calcd. for $C_{21}H_{28}NOI$: N, 3.20. Found: N, 3.17, 3.10.

Oxalate (from absolute ethanol), m.p. 161.5–163°; reported for Isoamidone I oxalate,[2] 158–160°.

Anal. Calcd. for $C_{20}H_{25}NO \cdot C_2H_2O_4$: N, 3.65. Found: N, 3.60.

Picrate (from ethanol) m.p. 134–136°; reported for Isoamidone I picrate,[2] 131–133°.

Anal. Calcd. for $C_{26}H_{28}N_4O_8$: N, 10.68. Found: N, 10.48, 10.52.

Acknowledgment.—The authors wish to thank Dr. Joseph R. Stevens, Technical Director of the J. T. Baker Chemical Company, for permission to publish the results of some experiments carried out in the research laboratory of the J. T. Baker Chemical Company, Phillipsburg, New Jersey.

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[1] Abstracted in part from the thesis submitted in partial fulfillment of the requirements for the degree of doctor of philosophy.

[2] N. R. Easton, J. H. Gardner and J. R. Stevens, THIS JOURNAL, **70**, 76 (1948).

[3] D. J. Dupre, J. Elks, B. A. Hems, K. N. Speyer and R. M. Evans, *J. Chem. Soc.*, 500 (1949).

[4] M. Bockmühl and G. Ehrhart, *Ann.*, **561**, 52 (1948), [illegible] 173–175°.

The Rate of the Reaction between Thallium(III) and Iron(II) in Perchloric Acid Solution

BY OTTO L. FORCHHEIMER[1] AND ROBERT P. EPPLE

RECEIVED JUNE 30, 1952

While preparing a paper describing our work[2] on the kinetics of the Fe(II)–Tl(III) reaction, the article by Johnson[3] on the same subject appeared. We are therefore limiting our report to results which amplify or supplement those reported by him. Measurements made under the same conditions agree quantitatively.

Experimental

The preparation of the thallous, thallic, ferrous and ferric perchlorates has been previously described.[4] The perchloric acid was G. F. Smith Chemical Company's 70% "purified." Spot tests as recommended by Feigl[5] showed that this acid had a ferric ion content of less than $3 \times 10^{-6}F$ and a chloride ion concentration of less than 3×10^{-5}. No chlorate could be detected. The ferrous perchlorate stock solution contained traces of chloride ion (for quantitative information see reference 4), but not in sufficient amounts to affect the results of this investigation. Sodium and lithium perchlorates were prepared by adding the reagent grade carbonate to perchloric acid. Basic magnesium carbonate was used in the same manner to prepare a magnesium perchlorate solution. Manganese perchlorate solutions were prepared by dissolving the reagent grade metal in perchloric acid. These solutions all contained less than the above limits of iron and chloride ion. All other chemicals used were Baker and Adamson reagent grade.

The reactants, in separate glass-stoppered bottles, were allowed to come to uniform temperature in a constant temperature bath. The order of addition did not affect the results. All experiments were carried out at 25 ± 0.1°. The time of starting a run was taken at the time when one half of the second reagent had been added to the first. Samples for analysis were taken with a pipet and discharged into an acidic chromate solution which stopped the reaction by oxidizing iron(II) and precipitating thallium(I). The acidic precipitate was metathesized into the stoichiometric thallous chromate by a previously described method.[4]

Although chloride ion has been mentioned as a catalyst for the dichromate oxidation of thallium(I),[6] tests showed

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[1] University of Chicago, Chicago, Ill.

[2] O. L. Forchheimer, Thesis, Brown University, 1951.

[3] C. E. Johnson, Jr., THIS JOURNAL, **74**, 959 (1952).

[4] O. L. Forchheimer and R. P. Epple, *Anal. Chem.*, **23**, 1445 (1951).

[5] F. Feigl, "Qualitative Analysis by Spot Tests," Nordemann Publishing Co., Inc., New York, N. Y., 1939, pp. 97–98, 161.

[6] P. A. Shaffer, *Cold Spring Harbor Symposia Quant. Biol.*, **7**, 50 (1939).