TABLE I

2-HYDROXY-3-ALKYLQUINOXALINES

R	M.p., °C. uncor.	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found	Absorption maxima and mol. extinction coefficients λ, mμ ($\epsilon \times 10^{-3}$) 0.1 *N* NaOH	0.1 *N* HCl	95% Ethanol
$-CH_2CH_2CH_3$	184–185	15	14.88	14.94 14.85	238(26.32)	229(19.69) 254(7.28) 290(5.98)	230(20.86) 280(6.01)
$-CH_3(CH_3)_2$	233–234	14	14.88	15.06 14.75	238(24.67)	228(18.51) 252(6.42) 288(5.46)	229(21.75) 279(6.18)
$-(CH_2)_3CH_3$	154–155	34	13.85	13.78 13.72	238(24.69)	228(18.40) 252(6.88)	229(21.73) 280(6.28)
$-(CH_2)_4CH_3$	151–152	8	12.95	12.70 13.06	238(26.39)	228(19.15) 252(6.54)	229(22.39) 280(6.65)
$-(CH_2)_5CH_3$	140–141	31	12.16	12.11 12.25	238(27.51)	Very insoluble	230(21.40) 280(6.31)

Both Motylewski[3] and Hinsberg[6] demonstrated that *o*-phenylenediamines and α-haloacids could be condensed to give mixtures of various products, including 2-hydroxy-3-alkyl-3,4-dihydroquinoxaline and its oxidation product, 2-hydroxy-3-alkylquinoxaline. More recently, Wear and Hamilton[7] showed that a basic solution of hydrogen peroxide was an excellent reagent for the oxidation of 2-hydroxy-3-alkyl-3,4-dihydroquinoxalines to 2-hydroxy-3-alkylquinoxalines. The 2-hydroxy-3-alkylquinoxalines reported in this paper were prepared by combining the above methods into one general reaction, giving colorless crystalline products which were soluble in basic solutions, moderately soluble in organic solvents, and relatively insoluble in water and acid solutions.

Table I lists the physical properties and ultraviolet absorption characteristics of the new compounds prepared.

Experimental Procedures

2-Hydroxy-3-alkylquinoxalines. General Procedure.—Into a 1-l., three-necked flask equipped with a reflux condenser and paddle stirrer were placed 10.8 g. (0.1 mole) of *o*-phenylenediamine and 0.066 mole of α-haloacid. The contents of the flask was stirred and heated on a steam-bath for 8 hours, then to this solution was added 8 g. of sodium hydroxide, 100 ml. of water and 10 ml. of 30% hydrogen peroxide solution. Heating and stirring were continued an additional 4 hours. The solution was treated with 1 g. of charcoal and filtered hot.

The cooled filtrate was extracted with three 100-ml. portions of ether to remove undesired tars; all ether extractions were discarded. The filtrate was then heated on a steam-bath to drive off any ether which still remained in solution, and the cooled filtrate was brought to *p*H 4 with acetic acid, whereupon the 2-hydroxy-3-alkylquinoxaline precipitated as a tan powder in 50 to 80% yield, melting approximately 25–30° below the melting point of the pure material.

The crude material was purified for analysis by sublimation at 1 mm. and at a temperature about 10° below the crude melting point, recrystallized 4 times from hot 95% ethanol, and again sublimed to give white crystals (except 2-hydroxy-3-*n*-butylquinoxaline which remained a light yellow in color despite repeated recrystallizations from dioxane, acetone and benzene, in addition to the alcohol recrystallizations) in 8 to 34% yield.

Absorption Spectra.—The ultraviolet absorption spectra, condensed in Table I, were obtained on a Beckman Model DU quartz spectrophotometer.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MIAMI
CORAL GABLES, FLORIDA

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Addition Compounds of Silicon Tetrachloride with Amides

BY KURT GINGOLD[1] AND EUGENE G. ROCHOW

RECEIVED SEPTEMBER 3, 1953

Silicon tetrachloride is unusual in the paucity of addition compounds it forms. Ammonia appears to ammonolyse it, and only amines form compounds with integral molar ratios. Three such amine adducts have been known for over fifty years,[2,3] and many more have recently been described in a thorough series of investigations by Trost[4–8]: all contain one, two or four moles of amine per mole of silicon tetrachloride. Trost also reports that silicon tetrachloride forms addition compounds with ketones, acids, esters and alcohols,[8] but gives no information about the composition or structure of such substances. An unsuccessful attempt to prepare addition compounds of silicon tetrachloride with amides was reported by Harold,[9] who passed the vapor of the tetrachloride into some fused amides and observed no combination. Despite the affinity of silicon for oxygen, compounds of silicon tetrachloride with oxygen-containing substances are still more rare: the compounds with ether, dioxane, tetrahydrofuran and tetrahydropyran that might have been anticipated have not been obtained.[10–12]

We now find that compounds of the formulas $SiCl_4 \cdot 10HCONH_2$ and $SiCl_4 \cdot 5HCON(CH_3)_2$ may be prepared by mixing solutions of the components in anhydrous organic solvents. These compounds are white solids and are quite stable in the absence of moisture. They are somewhat soluble in excess of the amide but are insoluble in common organic solvents. The bonding between the central silicon

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[1] Procter and Gamble Predoctoral Fellow at Harvard University, 1952–1953.

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[3] F. Lengfeld, *Am. Chem. J.*, **21**, 531 (1899).

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[10] H. H. Sisler, H. H. Batey, B. Pfabler and R. Mattair, *ibid.*, **70**, 3824 (1948).

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atom and the ligands in these compounds is believed to be through the nitrogen atom, but evidence on this point must await structural studies which are being undertaken in this Laboratory. The unusually high molar ratio found in the compound with formamide, $SiCl_4 \cdot 10HCONH_2$, may be due to the presence of dimeric molecules of the amide.

Experimental

Dried formamide (water content, as determined by titration with Karl Fischer reagent = 0.1%), dried dimethylformamide (water content = 0.01%) and purified-grade (99.8%) silicon tetrachloride were used.

Several samples of each compound were prepared by mixing dilute solutions of the components in anhydrous acetone, ether or benzene as solvents. The addition compound in each case was filtered off, washed well with the solvent, and dried for several days in an Abderhalden drying pistol, under refluxing acetone, at a pressure of 10–15 mm. It was necessary to carry out all transfers of materials in a dry-box in an atmosphere of dry nitrogen to prevent hydrolysis of the addition compounds.

Analyses of the dry compounds are given below. Chlorine was determined by titration of chloride ion with silver nitrate in neutralized aqueous solution. Silicon was determined as silica by ignition after hydrolysis with distilled water. Carbon and hydrogen analyses by combustion were performed by the microanalytical laboratory of the Massachusetts Institute of Technology.

Anal. Calcd. for $SiCl_4 \cdot 10HCONH_2$: C, 19.36; H, 4.88; Cl, 22.86. Found: C, 19.25; H, 5.16; Cl, 22.53, 22.53 (mean = 22.53). Calcd. for $SiCl_4 \cdot 5HCON(CH_3)_2$: C, 33.68; H, 6.59; Si, 5.25; Cl, 26.51. Found: C, 33.61; H, 6.44; Si, 5.29, 4.99 (mean = 5.14); Cl, 26.89, 26.84, 26.87 (mean = 26.87).

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HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

Preparation and Properties of 1-Bromo-1-propyne, 1,3-Dibromopropyne and 1-Bromo-3-chloro-1-propyne[1,2]

BY LEWIS F. HATCH AND LOUIS E. KIDWELL, JR.

RECEIVED AUGUST 3, 1953

The preparation of 1-bromo-1-propyne by the dehydrobromination of 1,1,2-tribromopropane has been reported[3] but the analysis of the product was sufficiently in error to cast serious doubt upon the purity of the 1-bromo-1-propyne (Calcd. for C_3H_3Br: Br, 67.2. Found: Br, 55.6, 57.7, 56.3). The only other reference to the synthesis of 1-bromo-1-propyne is that of Cleveland and Murray[4] who prepared it by the reaction between propyne and potassium hypobromite.[5] They characterized their product by its boiling point and Raman spectrum.

1,3-Dibromopropyne has been prepared by Lespieau[6] by the dehydrobromination of 1,2,3-tribromopropene.

1-Bromo-1-propyne, 1,3-dibromopropyne and 1-bromo-3-chloro-1-propyne have now been synthesized by the treatment of the appropriate acetylenic compound with an aqueous, alkaline solution of potassium hypobromite. The 1-bromo-1-propyne had a boiling point in agreement with previously reported boiling points but a density different from that given by Loevenich, Losen and Dierichs.[3] It was not possible to obtain an index of refraction because 1-bromo-1-propyne is spontaneously flammable in air. The infrared spectrum of the 1-bromo-1-propyne is in close agreement with the Raman spectrum obtained by Cleveland and Murray.[4] There was no indication of an acetylene–allene rearrangement which would have been evident by a sharp allene band at 5.1 μ.[7]

Both the 1,3-dibromopropyne and the 1-bromo-3-chloro-1-propyne were obtained in good yields with very little rearrangement to the corresponding allene. The spectrum of the dibromide showed a weak band at 5.08 μ indicating the presence of a small amount of dibromopropadiene.

$$Br{-}C{\equiv}C{-}CH_2Br \rightleftarrows BrHC{=}C{=}CHBr$$

The same band (5.10 μ) with the 1-bromo-3-chloro-1-propyne was very weak. This decreased tendency for a chloride to undergo rearrangement in the acetylene–allene rearrangement is similar to allylic rearrangement toward which chlorides are more stable than are the bromides.

The unexplained band near 5.85 μ found in the spectra of some propargyl halides was completely absent in the spectra of 1,3-dibromopropyne and 1-bromo-3-chloro-1-propyne. This is similar to the observations of Jacobs and Brill[7] on the spectra of 3-chloro-1-propyne where it was absent and 3-bromo-1-propyne where it was very weak and at 5.7 μ. All three of the 1-bromo compounds showed a strong, sharp $—C{\equiv}C—$ band at 4.48 μ, (4.50 μ for 1-bromo-3-chloro-1-propyne) but no band at 4.65 μ, the $—C{\equiv}C—$ stretching frequency found in the 3-halopropynes. There was also a strong band at 6.95 μ for 1-bromo-1-propyne, 7.01 μ for 1,3-dibromopropyne and 6.99 μ for 1-bromo-3-chloro-1-propyne.

The usefulness of the hypobromite ion in the preparation of 1-bromo-1-alkynes lies not only in the better yields obtained but also in the mild conditions employed which minimizes rearrangement into the isomeric allene. This same type of reaction was tried using hypochlorite ion with propyne, 3-bromo-1-propyne and 3-chloro-1-propyne but without success.

Experimental

1-Bromo-1-propyne.—The 1-bromo-1-propyne was prepared by the reaction between propyne and hypobromite ion.[4] The hypobromite ion solution was formed by the treatment of 2.68 moles of potassium hydroxide in 1 liter of water at *ca.* 5° with 0.67 mole of bromine. The propyne (Research Grade, Farchan Research Laboratories) was slowly passed through this cold solution until all of the hypobromite ion had reacted. The 1-bromo-1-propyne was extracted using diethyl ether and dried over magnesium sulfate.

The 1-bromo-1-propyne was distilled under an atmosphere of nitrogen to give a 75% yield based on the hypobromite ion; b.p. 64–65° (750 mm.), $d^{20}{}_4$ 1.5325, $d^{25}{}_4$ 1.5222, $d^{30}{}_4$ 1.5122; lit.[3] b.p. 65°, $n^{25}{}_D$ 1.44482, $d^{25}{}_0$ 1.35015.

Anal. Calcd. for C_3H_3Br: Br, 67.2. Found: Br, 67.2, 67.1.

1,3-Dibromopropyne.—The 1,3-dibromopropyne was prepared by the treatment of 0.67 mole of 3-bromo-1-propyne

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[1] This research was supported by the United States Air Force under Contracts No. AF 33(038)-21745 and No. AF 18(600)-430.

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