described for digermane. The separation was conducted at 185° at a flow rate of 450 ml./min. of helium and yielded triethylsilyltriethylgermane of 99.9% purity or better, the retention time being 54.2 min.

Anal. Calcd. for $C_{12}H_{30}SiGe$: C, 52.40; H, 10.99; mol. wt., 275. Found: C, 52.15; H, 10.89; mol. wt., 279 (osmometric).

The other properties of this compound are shown in Table I and are compared with those of hexaethyldisilane and hexaethyldigermane.

Repetition of this experiment with periodic removal of aliquots which were analyzed by gas phase chromatography showed that hexaethyldigermane was formed first, the mixed metal compound second, and the disilane was formed last.

Two subsequent runs were made employing 0.19 mole of triethylbromogermane, 0.19 mole of triethylbromosilane, and 0.48 g.-atom of sodium at 175–230° for 2 days, and 0.23 mole of triethylbromogermane, 0.23 mole of triethylbromosilane, and 0.43 g.-atom of sodium at 175–195° for 8 days. In the first of these runs, 38 g. of high boiling product was obtained consisting of 7% by weight $[Et_2SiO]_4$, 28% by weight $Et_3SiSiEt_3$, 21% by weight $Et_3SiGeEt_3$, and 44% by weight $Et_3GeGeEt_3$. In the second run, 35 g. of high boiling product was obtained consisting of 19% by weight $[Et_2SiO]_4$, 7% by weight $Et_3SiSiEt_3$, 21% by weight $Et_3SiGeEt_3$, and 54% by weight $Et_3GeGeEt_3$.

Attempted Preparation of Hexaethyldisilane.—A mixture of 19.5 g. (0.10 mole) of triethylbromosilane, 50 ml. of tetrahydrofuran and 2.1 g. (0.30 g.-atom) of lithium was refluxed under argon overnight. The slightly colored mixture was then added to diethyl ether, filtered to remove lithium bromide, and distilled to yield several products, b.p. 65–130° (50–0.3 mm.). The infrared spectrum of each of the two major fractions, b.p. 82–90° (0.3 mm.) and 104–115° (0.3 mm.), $n^{25}D$ 1.4465, had strong bands at 9.25 and 10.0 μ, indicative of the presence of C–O–C and Si–O–C groups, respectively. There were no bands indicative of OH groups in the 3-μ region. The molecular weights (ebulliometric in chloroform) were 215 and 250, respectively. The higher boiling fraction had the following analysis consistent with that calculated for 4-triethylsiloxy-*n*-butyl ether.[4]

Anal. Calcd. for $C_{14}H_{32}O_2Si$: C, 64.56; H, 12.39, mol. wt. 260. Found: 64.22; H, 12.99; mol. wt., 250 (ebulliometric).

Attempted Preparation of Triethylsilyltriethylgermane by Cleavage of Hexaethyldigermane.—A mixture of 17.8 g. (0.056 mole) of hexaethyldigermane, 23 g. (0.118 mole) of triethylbromosilane, and 1.1 g. (0.048 g.-atom) of sodium was refluxed for 24 hr. Analysis of an aliquot indicated the presence of a small amount of the disilane with none of the mixed-metal compound present. Two additional increments of 1.1 g. (0.048 g.-atom) of sodium were then added in 24-hr. intervals while continuing to reflux the reaction mixture. Analysis after each of these 24-hr. intervals indicated that the disilane content increased with no change in the digermane content. In no case was there any evidence for the presence of triethylsilyltriethylgermane by gas phase chromatography.

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Chlorination of 2,3-Dimethylpyrazine

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Upon reinvestigation of the reaction of chlorine and 2,5-dimethylpyrazine, Hirschberg and Spoerri[3] found that a rapid, exothermic reaction took place, even in the absence of light, to yield 2-chloro-3,6-dimethylpyrazine. 2-Methylpyrazine was found to undergo a similar reaction to yield 2-chloro-3-methylpyrazine. When the reaction was extended to 2,6-dimethylpyrazine, however, it was found that the reaction proceeded extremely slowly until the solution was irradiated with ultraviolet light. The product of this reaction was shown to be the unstable 2,6-bis-(α-chloromethyl)-pyrazine. Accordingly, it seemed of interest to extend this work to the remaining dimethyl isomer, 2,3-dimethylpyrazine (I). This compound was prepared by a sequence of reactions first described by Gabriel and Sonn[4] in 1907.

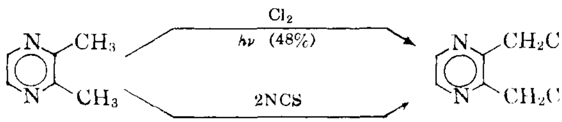
However, in order to obtain high yields of I several modifications of Gabriel's procedure were necessary. The preparation is described in the experimental part. A number of attempts to prepare I according to a recent procedure by Ishiguro and Matsumura[5] gave unsatisfactory yields.

In the manner specified by Hirschberg and Spoerri,[3] chlorine was rapidly bubbled through a solution of I in carbon tetrachloride in the absence of light. After an initial evolution of heat, no precipitate was observed to form. Passage of chlorine was continued for an additional 20 min. after which only a small amount of a white precipitate had formed. The solution was then illuminated with ultraviolet light and the passage of chlorine resumed. This apparently speeded the reaction for within 20 min. a substantial amount of a white solid precipitated. In order to insure completeness of the reaction, the passage of chlorine was continued for an additional 100 min. Examination of the white precipitate showed it to be a hydrochloride of I.

Evaporation of the carbon tetrachloride filtrate left a residual, lachrymatory oil, which polymerized to a tacky solid on standing and which could not be distilled. By analogy with the α-chloromethylpyrazines[3] it seemed that this material was 2,3-bis-(α-chloromethyl)pyrazine (II) and, accordingly, it was treated with an excess of sodium ethoxide in absolute ethanol.

The stable liquid obtained from this alcoholysis exhibited a strong peak in the infrared at 1102 cm.$^{-1}$ consistent with an aliphatic ether.[6] Elemental analysis showed it to be a bisether and, hence, that the oil originally obtained was 2,3-bis-(α-chloromethyl)pyrazine.

In order to verify this, I was treated with two equivalents of N-chlorosuccinimide and a catalytic amount of benzoyl peroxide in carbon tetrachloride. The unstable, lachrymatory oil thus obtained afforded the same bisether previously obtained as shown by a comparison of their infrared spectra.



I II

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[1] (a) The work herein reported is based on a thesis submitted by Robert A. Pages in partial fulfillment of the requirements for the degree of Bachelor of Science (Chemistry) at the Polytechnic Institute of Brooklyn, June, 1962; (b) National Science Foundation Undergraduate Summer Research Program participant, 1961.

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[3] A. Hirschberg and P. E. Spoerri, *J. Org. Chem.*, **26**, 2356 (1961).

[4] S. Gabriel and A. Sonn, *Ber.*, **40**, 4855 (1907).

[5] T. Ishiguro and M. Matsumura, *Yakugaku Zasshi*, **78**, 229 (1958); *Chem. Abstr.*, **52**, 11862a (1958).

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For purposes of comparison, the monoethyl ether was also prepared with one equivalent of N-chlorosuccinimide and alcoholysis of the resulting unstable, lachrymatory oil. The stable liquid thus obtained exhibited a strong peak in the infrared at 1100 cm.$^{-1}$ consistent with an aliphatic ether.[6] This was verified by elemental analysis.

Experimental[7]

A. **2,3-Dimethylquinoxaline.**—In 2 l. of 2.5% acetic acid, 135 g. of *o*-phenylenediamine (1.25 moles) was dissolved at 65°. A solution of 107.6 g. of biacetyl (1.25 moles) in 750 ml. of water was added, with stirring, over a period of 15 min. The mixture was stirred for an additional 15 min., neutralized with 20% potassium hydroxide, and allowed to stand overnight at 5°. The crude product was filtered, washed with cold water, and recrystallized from aqueous ethanol after treatment with Norit. The product, which crystallizes as the dihydrate, was dried at 60° overnight and was found to weigh 180 g. (91%). It had a melting point of 105.5–106.5° (lit. m.p. 106°).

B. **5,6-Dimethylpyrazine-2,3-dicarboxylic Acid.**—2,3-Dimethylquinoxaline (40 g., 0.253 mole) was dissolved in 2 l. of water at 80° in a 3-l. flask fitted with an efficient stirrer and a thermometer. Potassium permanganate (240 g., 1.52 moles) was added in 3–5-g. portions with vigorous stirring at a rate sufficient to maintain the temperature at 85°. The addition required 1.5–2 hr. The reaction mixture was then stirred at 90° for an additional hour. The hot mixture was filtered and the cake of manganese dioxide washed with hot water until the test washings no longer gave a pink color with 1% ferrous sulfate solution. The combined filtrate and washings were evaporated to about 1 l. under reduced pressure and 126 ml. of 37% hydrochloric acid (1.52 moles) cautiously added with stirring. Evaporation under reduced pressure was continued until 500 ml. remained. The mixture was then cooled and the crude diacid–dihydrate removed by filtration. The filtrate was evaporated to dryness under reduced pressure. Fifty milliliters of water was added followed by 750 ml. of acetone and the mixture refluxed 15 min., filtered, and the filtrate evaporated to dryness. The resulting solid was dissolved by refluxing in 750 ml. of acetone, treated with Norit, filtered, and evaporated to dryness to yield the acid as a light tan crystalline solid. The crude product was recrystallized from water after treatment with Norit and dried in a vacuum desiccator over Drierite. The pure product weighed 34 g. (69%) and had a melting point of 192–193° dec. (lit.[8] m.p. 190°); neut. equiv., 98.51 (theoretical 98.08).

C. **Derivatives of 5,6-Dimethylpyrazine-2,3-dicarboxylic Acid.** 1. **Anhydride.**—Anhydrous acid (4.90 g., 0.025 mole) in 15 ml. of acetic anhydride was heated on a water bath for 4 hr., cooled at 0°, and filtered to yield 2.8 g. of colorless crystals having a melting point of 171–171.5°. Evaporation of the mother liquor followed by treatment with Norit yielded an additional 0.94 g. of anhydride; total yield, 3.74 g. (84%).

Anal. Calcd. for $C_8H_6N_2O_3$: C, 53.94; H, 3.40; N, 15.73. Found: C, 54.00; H, 3.48; N, 15.71.

2. **Methyl Hydrogen Ester.**—One gram of anhydride (0.006 mole) was refluxed in 5 ml. of absolute methanol for 15 min. and evaporated to dryness on a water bath. The residue was recrystallized from benzene–cyclohexane to yield 0.97 g. (82%) of colorless crystals melting at 107–107.5°; neut. equiv., 208.9 (theoretical 210.2).

Anal. Calcd. for $C_9H_{10}N_2O_4$: C, 51.43; H, 4.80; N, 13.33. Found; C, 51.38; H, 4.86; N, 13.31.

D. **2,3-Dimethylpyrazine.**—Anhydrous 5,6-dimethylpyrazine-2,3-dicarboxylic acid (58.9 g., 0.30 mole) was refluxed in 350 ml. of quinoline, under a stream of nitrogen, until no more carbon dioxide was evolved (approximately 4 hr.). The mixture was then carefully fractionated under vacuum to yield 30.2 g. (93%) of 2,3-dimethylpyrazine (I) boiling at 45–46.5° (11 mm.).

Physical properties: b.p. 155.5–156.5° (lit.[9] 156°); n^{20}_{D} 1.5076; d^{25}_{4} 1.005.

I was identified by preparation of a picrate, m.p. 149.5–150.5° (lit.[9] 150°).

A methiodide was prepared by a method given by Shriner, Fuson, and Curtin[10] which had m.p. 183–184°.

Anal. Calcd. for $C_7H_{11}N_2I$: N, 11.22. Found: N, 11.21.

E. **2-(α-Chloromethyl)pyrazines.** 2-(α-Chloromethyl)-3-methylpyrazine and 2,3-bis(α-chloromethyl)pyrazine (II) were prepared by the reaction of N-chlorosuccinimide with an equimolar quantity of 2,3-dimethylpyrazine (I), using a catalytic amount of benzoyl peroxide (procedure A). In addition, 2,3-bis(α-chloromethyl)pyrazine (II) was also prepared by treatment of I with chlorine in the presence of ultraviolet light (procedure B).

These α-chloromethylpyrazines are unstable, lachrymatory oils, which decompose on standing, and could not be purified by fractional distillation. Accordingly, after isolation, they were immediately used in the preparation of the corresponding pyrazinylmethyl ethyl ethers.

Procedure A. All (α-Chloromethyl)pyrazines.—I (5.4 g., 0.05 mole) in 250 ml. of carbon tetrachloride containing 1 or 2 equivalents of N-chlorosuccinimide and 0.1 g. of benzoyl peroxide was refluxed 12 hr., cooled to 0°, filtered, and the residue washed with two additional 25-ml. portions of carbon tetrachloride. The combined filtrate and washings were evaporated under vacuum at room temperature. The residual oils were immediately used for the preparation of the corresponding ethyl ethers. The yields of these oils ranged from 75–80% (assuming the oils to be pure).

Procedure B. 2,3-Bis-(chloromethyl)pyrazine.—To 250 ml. of carbon tetrachloride was added 10.8 g. of I (0.1 mole). Chlorine was rapidly bubbled in through a sintered glass gas addition tube while the flask was irradiated with ultraviolet light (Burdick-Type QA-250N). A white precipitate formed after only a few minutes. The passage of chlorine was continued for 2 hr. The mixture was then filtered and the residue washed with two 50-ml. portions of fresh carbon tetrachloride. The filtrate and washings were evaporated under reduced pressure leaving 4.0 g. II as a yellow oil which was immediately used in the preparation of the corresponding ethyl ether. A 23% conversion to II was obtained, based on recovery of 5.6 g. I from its hydrochloride. The yield was 48% (assuming the oil to be pure).

F. **2,3-Bispyrazinylmethyl Ethyl Ether.**—To 0.12 mole of sodium ethoxide in 200 ml. of absolute ethanol was added 0.035 mole of II (6.2 g.) in 25 ml. of absolute ethanol and the mixture refluxed 12 hr., cooled, filtered, and the residue of sodium chloride washed with several portions of absolute ethanol. The combined filtrate and washings were diluted with 25 ml. of water and concentrated on a water bath until most of the alcohol had been removed. The residual oil was then extracted from the alkaline, aqueous layer with diethyl ether. The ether extracts were dried over anhydrous magnesium sulfate and concentrated on a water bath. The residual oil was then carefully fractionated to yield 1.4 g. (20%) of the bisethyl ether which had a boiling point of 115–116° (10 mm.), n^{20}_{D} 1.4890.

Anal. Calcd. for $C_{10}H_{16}N_2O_2$: C, 61.20; H, 8.22; N, 14.27. Found; C, 61.15; H, 8.31; N, 14.41.

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[7] All melting points are corrected. Infrared spectra were determined on a Perkin-Elmer Infracord spectrophotometer. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., or by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

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The Cleavage of Aryl Ethers by Alkali Metals in Aliphatic Ether Solvents. Detection by Electron Spin Resonance[1]

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The cleavage of aryl ethers by alkali metals in inert solvents at room temperature was detected by electron

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