that the bromination of furoic acid produced an 84–85° melting $C_4H_3BrO_2$ compound has not been resolved. However, our first experiment provided a few crystals of a substance (m.p. 84°) whose infrared and ultraviolet spectra were identical to those observed for β-bromocrotonolactone which was isolated in all other experiments. This suggests that the higher melting product may be a polymorphic crystalline form of β-bromocrotonolactone.

Hodgson and Davies[3b] described their compound (m.p. 85°) as 2-bromo-3-hydroxyfuran and reported its reduction to an unauthenticated product, 3-hydroxyfuran. If 3-hydroxyfuran were actually the product, it would probably exist in its tautomeric keto form in accordance with results observed by Eugster and coworkers[5] regarding the keto–enol equilibrium of related compounds. Limpricht[3a] also reduced his bromo compound but did not obtain sufficient quantities to investigate the product. Only unidentified dark oils were produced when the reduction procedures of Hodgson and Davies[3b] were applied to β-bromocrotonolactone.

The identity of our 78° melting bromo compound was established by comparing its properties with those observed for an authentic sample of β-bromocrotonolactone prepared by hydrobromination of hydroxytetrolic acid.[6] The small coupling constant ($J = 1.8$ c.p.s.) between the α and γ-hydrogens observed in the n.m.r. spectrum[7] of β-bromocrotonolactone supports the previous assignment[2b,8] of the bromine to the β-position in this isomer. The α-hydrogen appeared as a triplet centered at $3.67\ \tau$ while the two γ-hydrogen gave rise to a doublet at $5.14\ \tau$.

4-Bromo-2-furoic acid[4a,9] may be an intermediate in the conversion of furoic acid to β-bromocrotonolactone. Hill and Cornelison[10] demonstrated that the action of bromine water on 4-bromo-2-furoic acid produced β-bromocrotonolactone, while the isomeric α-bromocrotonolactone was formed from the treatment of 4,5-dibromo-2-furoic acid,[8a,9] with hydrobromic acid. The bromination of furoic acid may initially produce a small amount of 4-bromo-2-furoic acid which might be converted to β-bromocrotonolactone during the steam distillation.

In some experiments the crude products obtained from the bromination of furoic acid were not submitted to steam distillation but were worked up directly. In these instances bromofuroic acids corresponding to those reported by Bailey and Waggoner[4] were found.

Experimental

Bromination of 2-Furoic Acid.—Ten grams of furoic acid (m.p. 133°) was mixed with 10 ml. of water. Following Hodgson and Davies' procedure,[3b] the paste was stirred vigorously at 28–30° for 40 min. during the addition of 30 g. of bromine. After stirring the mixture for an additional 20 min., it was dissolved in 100 ml. of water and steam distilled. Extraction of the first 500 ml. of distillate with three 100-ml. portions of ether afforded, on evaporation, 340 mg. (3% yield) of β-bromocrotonolactone, m.p. 78°; $\lambda_{max}^{H_2O}$ 224.5 mμ (ϵ 13,500); $\nu_{max}^{CS_2}$ 1782, 1609, 1470, 1250, 1140, 1020, 860, and 758 cm.$^{-1}$.

The same product (m.p. 78°) was also obtained in low yield when the reaction was carried out by Hodgson and Davies' alternate procedure[3b] using chloroform as the reaction medium.

Our β-bromocrotonolactone showed no depression in melting point when mixed with a sample of β-bromocrotonolactone prepared by the method of Lespieau and Viguier[6] (see following); the β-anilino derivative[10] of our compound, m.p. 217–219°, agrees in melting point with that of the β-anilino derivative from the Lespieau and Viguier preparation (217–218° [10]; 220° [11]).

In the first experiment using the chloroform reaction medium a few crystals of an 84° melting substance were obtained from the ether extract of the steam distillate. This compound was characterized only by infrared (carbon disulfide) and ultraviolet (water) spectra which were identical in all respects to those observed later for β-bromocrotonolactone. Lack of material prevented further investigation of this compound.

When the product obtained from the bromination of furoic acid in water was not steam distilled but rather allowed to stand overnight in 100 ml. of water, crystals were obtained, m.p. 186–187°, corresponding to the 5-bromo-2-furoic acid (m.p. 186–187°) isolated by Bailey and Waggoner.[4] Similarly, the crude product from the bromination in the chloroform medium was dissolved in an ether–petroleum ether solution. On cooling this solution, a crystalline product (m.p. 158–160°) was obtained which corresponds to the 2,3,4,5-tetrabromotetrahydro-2-furoic acid (m.p. 159–160°) isolated by Bailey and Waggoner[4] from a similar reaction.

Attempts to Reduce β-Bromocrotonolactone.—β-Bromocrotonolactone was submitted to Hodgson and Davies' reduction procedure[3b] using 30% aqueous sodium hydroxide and 2.5% sodium amalgam and alternatively, sodium and ethyl alcohol. In both instances only a small amount of a dark brown oil, not characterized, was obtained.

β-Bromocrotonolactone from Hydroxytetrolic Acid.—Propargyl alcohol (16.8 g., b.p. 112–114°) was converted to hydroxytetrolic acid (13.3 g., m.p. 115–116°) by the procedure developed by Haynes and Jones[12] and modified by Henbest, Jones, and Walls.[13] Hydrobromination of hydroxytetrolic acid (10 g.) by Lespieau and Viguier's method[6] produced β-bromocrotonolactone (12.1 g.), m.p. 78°.

Acknowledgment.—The author expresses his thanks to Dr. M. G. Ettlinger for his helpful guidance during the course of this work.

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(5) C. H. Eugster, R. E. Rosenkranz, K. Allner, and A. Hofmann, *Angew. Chem.*, **73**, 737 (1961).

(6) R. Lespieau and P. L. Viguier, *Compt. rend.*, **146**, 295 (1908); **148**, 419 (1909).

(7) For this n.m.r. spectrum the author is indebted to Dr. J. C. Davis, Jr., of the Department of Chemistry, University of Texas. The spectrum was taken in dueteriochloroform on the Varian HR-60 spectrometer using tetramethylsilane as an internal reference.

(8) The controversy regarding the position of the bromine in the two isomeric bromocrotonolactones (m.p. 58° and m.p. 78°) was clarified by (a) R. J. Vander Wal, *Iowa State Coll. J. of Sc.*, **11**, 128 (1936–37) [*Chem. Abstr.*, **31**, 2207 (1937)]; (b) M. C. Whiting, *J. Am. Chem. Soc.*, **71**, 2946 (1949); (c) L. N. Owen and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3105 (1949); (d) K. Sukigara, Y. Hata, Y. Kurita, and M. Kubo, *Tetrahedron*, **4**, 337 (1958); (e) Y. Hata, S. Senoh, and M. Murakami, *Nippon Kagaku Zasshi*, **79**, 1531 (1958) [*Chem. Abstr.*, **54**, 24620 (1960)]; (f) M. Murakami, S. Senoh, and Y. Hata, *Mem. Inst. Sci., Ind. Res. Osaka Univ.*, **16**, 219 (1959) [*Chem. Abstr.*, **54**, 22555 (1960)].

(9) The question relating to the position of the bromine in these substituted furoic acids was resolved by: (a) H. Gilman and G. F. Wright, *Chem. Rev.*, **11**, 323 (1932); (b) H. Gilman, R. J. Vander Wal, R. A. Franz, and E. V. Brown, *J. Am. Chem. Soc.*, **57**, 1146 (1935).

(10) H. B. Hill and R. W. Cornelison, *Am. Chem. J.*, **16**, 188, 277 (1894).

(11) L. Wolff and W. Schimpff, *Ann.*, **315**, 151 (1901).

(12) L. J. Haynes and E. R. H. Jones, *J. Chem. Soc.*, 503 (1946).

(13) H. B. Henbest, E. R. H. Jones, and I. M. S. Walls, *ibid.*, 3646 (1950).

Triethylsilyltriethylgermane[1]

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We wish to report the synthesis and some properties of triethylsilyltriethylgermane which appears to be the

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first fully alkylated mixed-metal compound of group IV-A metals reported to date. The compound was prepared by a mixed Wurtz coupling reaction of triethylbromosilane, triethylbromogermane, and sodium, in the absence of solvent, and was separated and purified by gas phase chromatography.

In the reaction of equimolecular quantities of triethylbromosilane and triethylbromogermane in the presence of a slight excess of sodium, it was found that the first product produced was hexaethyldigermane, followed by triethylsilyltriethylgermane, and then hexaethyldisilane. The possibility that the triethylsilyltriethylgermane arises by cleavage of hexaethyldigermane was ruled out by examining the reaction of triethylbromosilane, hexaethyldigermane, and sodium at 230–260°. The only product produced was hexaethyldisilane with no evidence for the cleavage of the digermane. It appears, therefore, that in the reaction of triethylbromosilane, triethylbromogermane, and sodium, three coupling reactions compete to produce the digermane, mixed-metal compound, and the disilane in decreasing rates, respectively.

Hexaethyldigermane was prepared by coupling triethylbromogermane in the presence of lithium in tetrahydrofuran (THF). In an effort to prepare hexaethyldisilane by the same method, it was found that the major product consisted of tetrahydrofuran cleavage products containing silicon. Infrared, partial elemental analysis (C, H only), and molecular weight data on the two major components indicate they are butoxytriethylsilane derivatives.[4] This result contrasts with that reported for the reaction of triphenylsilyllithium with tetrahydrofuran where the major product is 4-triphenylsilylbutanol-1.[5] This difference can be accounted for in terms of the greater stability of the triphenylsilyl anion compared to the triethylsilyl anion. In particular, triethylsilyl bromide may undergo preferential nucleophilic attack by tetrahydrofuran rather than significant metalation. The apparent absence of tetrahydrofuran cleavage products in the reaction of triethylbromogermane with lithium in tetrahydrofuran may be due to the greater ease of forming triethylgermyllithium which, in turn, more rapidly attacks triethylbromogermane than tetrahydrofuran.

The properties of the three ethylated intermetallics are summarized in Table I. An interesting fact is that the molar refraction [R_D] of the mixed-metal compound is very close to the average for disilane and digermane values. Similarly, the infrared spectrum of the mixed-metal compound appears, in general, to be a composite between those of the disilane and digermane. Distinguishing differences can however be noted at 15.2–15.4 μ (broad band), 10.65 μ (shoulder), 8.55 μ (weak band), and at about 8.25 μ (shoulder) for triethylsilyltriethylgermane in the liquid state.

TABLE I

PROPERTIES OF HEXAETHYLATED DISILANE,[a] SILYLGERMANE, AND DIGERMANE[a]

	B.p., °C. (760 mm.)	$n^{26}D$	d^{26}_4	[R_D]
$Et_3SiSiEt_3$	252.0	1.4771	0.8407	77.49
$Et_3SiGeEt_3$	254.5	1.4860	0.9791	80.65
$Et_3GeGeEt_3$	266.3	1.4952	1.1168	83.48

[a] Literature values: $Et_3SiSiEt_3$, b.p. 251.7° (760 mm.), $n^{20}D$ 1.4790; $Et_3GeGeEt_3$, b.p. 265° (760 mm.). H. C. Kaufman, "Handbook of Organometallic Compounds," D. Van Nostrand Company, Inc., 1961, pp. 617, 742.

Experimental[6]

Hexaethyldigermane.—Two methods were used. The first method consisted of refluxing triethylbromogermane and sodium for 6 days followed by distillation of the product.[7] Triethylbromogermane was prepared in near quantitative yield by brominating tetraethylgermane in ethyl bromide with an equimolecular quantity of bromine. The second method, which was similar to that employed for the preparation of hexaphenyldisilane,[8] consisted of reacting triethylbromogermane with lithium in tetrahydrofuran. To a solution of 12.0 g. (0.05 mole) of triethylbromogermane in 50 ml. of tetrahydrofuran was added 0.35 g. (0.05 g.-atom) of lithium under argon. After dissolution of the lithium, the mixture was refluxed about 6 hr. The tetrahydrofuran was removed at this point and the mixture heated until the pot temperature rose to 212° (2 hr.). The product was distilled *in vacuo* to yield 5 g. (63% yield) of hexaethyldigermane, b.p. 69–72° (0.1 mm.). Hexaethyldigermane was then purified to 99.9% purity or better by gas phase chromatography employing a 244 cm. long × 1.65 cm. i.d. preparative scale column packed with regular grade Chromosorb W (60–80 mesh) containing 20% by weight of a silicone rubber gum stock coating (Union Carbide, W95). The column was programmed to rise from 50–200° at a rate of 7.9°/min. (75 ml./min. helium flow). The retention time at 200° was 33.0 min.

Anal. Calcd. for $C_{12}H_{30}Ge_2$: C, 45.10; H, 9.46; mol. wt., 320. Found: C, 44.8; H, 9.50; mol. wt., 321 (osmometric).

Hexaethyldisilane.—A mixture of 19.5 g. (0.10 mole) of triethylbromosilane and 5.8 g. (0.25 g.-atom) of sodium was refluxed for 24 hr. during which time the temperature rose from 160–210°. The excess sodium and sodium bromide were removed by filtration and the residue was distilled *in vacuo* to yield about 7 g. (60% yield) of hexaethyldisilane, b.p. 67–70° (0.5 mm.). Hexaethyldisilane then was purified by gas phase chromatography employing the column described for hexaethyldigermane. The retention time of hexaethyldisilane at 200° (75 ml./min. He flow) was 25.5 min.

Anal. Calcd. for $C_{12}H_{30}Si_2$: C, 62.53; H, 13.12. Found: C, 62.48; H, 13.25.

Triethylsilyltriethylgermane.—A mixture of 19.5 g. (0.10 mole) of triethylbromosilane, 24.0 g. (0.10 mole) of triethylbromogermane, and 5.3 g. (0.23 g.-atom) of sodium was refluxed with stirring under argon. The original pot temperature was 178° and this slowly rose to 225° over a period of 5 days. The mixture was then cooled, taken up in diethyl ether, and filtered to remove excess sodium and sodium bromide. The filtrate was concentrated and distilled *in vacuo* to yield 24 g. of a fraction, b.p. 76–86° (0.50–0.35 mm.). Analysis of this fraction by gas phase chromatography (5% silicone rubber on Chromosorb W) indicated the presence of four components: the first amounting to 4% by weight (retention time, 20.3 min.); the second 28% by weight (retention time, 25.5 min.); the third 27% by weight (retention time, 29.0 min.); and the fourth 42% by weight (retention time, 33.0 min.). The first component was tentatively identified as the cyclic tetramer of diethylsiloxane, $[Et_2SiO]_4$,[9] by infrared analysis and molecular weight determination, the second as hexaethyldisilane, and the fourth as hexaethyldigermane—the latter two having the same retention times as authentic samples of the two compounds. The third component was separated and repurified by gas phase chromatography employing the column

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[4] The indicated analytical evidence suggests that they are *n*-butoxytriethylsilane and its next higher homolog, 4-triethylsiloxybutyl *n*-butyl ether. One of the referees has suggested that the latter might instead be 4-triethylsiloxybutyltriethylsilane. Calcd. for $C_{16}H_{38}OSi_2$: C, 63.55; H, 12.63; mol. wt., 303.

(5) (a) H. Gilman, *et al.*, *WADC Technical Report*, 53-426, (June 1959); (b) H. Gilman and D. Wittenberg, *J. Am. Chem. Soc.*, **80**, 2677 (1958).

(6) All boiling points are uncorrected but were determined by the same method.

(7) C. A. Kraus and E. A. Flood, *J. Am. Chem. Soc.*, **54**, 1635 (1932).

(8) (a) M. V. George, D. J. Peterson, and H. Gilman, *ibid.*, **82**, 403 (1960); (b) H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. Ind.* (London), 1479 (1958).

(9) This product whose assignment is tentative was also present in the hexaethyldisilane preparation but not in that of hexaethyldigermane. Accordingly, it is believed to arise either from an impurity in the starting triethylbromosilane or by a catalytic breakdown of the silicone rubber packing.

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.

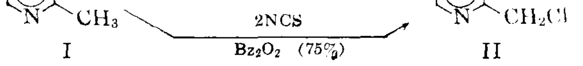
However, in order to obtain high yields of I several modifications of Gabriel's procedure were necessary. The preparation is described in the experimental part. A number of attempts to prepare I according to a recent procedure by Ishiguro and Matsumura[5] gave unsatisfactory yields.

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.



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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.

(2) To whom inquiries should be addressed.

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