unsaturated ketone, 9 ml. of ethanol, 50 mg. of 10% palladium-on-charcoal, and 1 ml. of 3*N* hydrochloric acid or 1 ml. of 10% aqueous potassium hydroxide was subjected to hydrogenation at room temperature under 1 atmosphere of hydrogen. After 1 mole of hydrogen was taken up the reaction stopped. The catalyst was removed by filtration, the solvent evaporated under reduced pressure, and the residue taken up in ether. The ether solution was washed neutral with saturated sodium chloride solution, dried, and evaporated. The residue was subjected to vapor phase chromatography as described above.

trans-7,7-Dimethyl-2-decalone. One gram of I ($R = CH_3$) in 20 ml. of anhydrous ether was added to 150 ml. of liquid ammonia. To this milky solution was added 100 mg. of lithium metal giving a persistant blue solution. The solution was stirred for 2 hr. and the reaction mixture decomposed by the addition of 5 g. of ammonium chloride. The ammonia was evaporated and the residue taken up in water. The aqueous solution was extracted with ether and the extracts dried and evaporated. Yield, 0.7 g.

The *2,4-dinitrophenylhydrazone* was recrystallized from ethanol, m.p. 164°–165°.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71. Found: C, 59.98; H, 6.66.

cis-7,7-Dimethyl-2-decalone. A mixture of 1 g. of I ($R = CH_3$), 20 ml. of ethanol, 2 ml. of 3*N* hydrochloric acid, and 100 mg. of 10% palladium-on-charcoal was subjected to hydrogenation at room temperature under 1 atmosphere of hydrogen. After hydrogen uptake ceased the catalyst was removed by filtration and the solvent evaporated under reduced pressure. The residue was taken up in ether and washed with saturated sodium chloride solution. The ether solution was dried and evaporated giving 0.8 g. of product.

The *2,4-dinitrophenylhydrazone* was recrystallized from 95% ethanol, m.p. 129°–130°.

Anal. Calcd. for $C_{18}H_{24}N_4O_4$: C, 59.98; H, 6.71. Found: C, 59.90; H, 6.79.

cis *2-Hydrindanone* was obtained from hydrogenation of IV[9] in acidic, basic, or neutral medium.

The semicarbazone was recrystallized from aqueous ethanol, m.p. 212°–213°. Reported m.p. 215°216°.[15]

cis *5-Hydrindanone* was obtained from hydrogenation of V[10] in acidic, basic, or neutral medium.

The *2,4-dinitrophenylhydrazone* was recrystallized from ethanol, m.p. 166°–167°. Reported m.p.'s 163°,[16] 163°–164°,[17] 168°–169°.[18]

The *semicarbazone* was recrystallized from aqueous ethanol, m.p. 195°–196°; reported melting points 203°,[16] 193°–195°,[17] 196°–197°,[18] 193°–195.5°.[19]

cis *3,5-Dimethylcyclohexanone* was obtained from hydrogenation of VI[11] in acidic, basic or neutral medium.

The *2,4-dinitrophenylhydrazone* was recrystallized from ethanol, m.p. 164°–165°; reported m.p. 166°–167°.[20]

The *semicarbazone* was recrystallized from aqueous ethanol, m.p. 200°–201°; reported melting points 206°–207°,[20] 200°,[21] 202°–203°.[22]

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[CONTRIBUTION FROM THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

Methioninemethylsulfonium Salts

KENICHI FUKUI, KATSUYOSHI KANAI, AND HISAO KITANO

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Methioninemethylsulfonium fluoborate was prepared. Its reaction with potassium salts of various acids afforded the corresponding sulfonium salts. Methioninemethylsulfonium perchlorate and fluosilicate were also prepared.

Only two existing methods are available for preparing DL-methioninesulfonium salts. One of the methods which affords sulfonium bromides and iodides as well as sulfates involves the interaction of alkyl halides[1-3] or sulfates[2,4,5] with methionine; while the other method which gives sulfonium chlorides[2] and acetates[2,4] employs anion exchange of sulfonium salts with the appropriate salts or acids.

Although the latter method has an advantage in that acetates and chlorides are obtainable which can never be prepared by the former method, an anion exchange method still has the limitations that intermediate sulfonium salts are prepared and purified with difficulty, and the desired sulfonium salts cannot easily be separated from the inorganic salts formed as a by-product.

During our investigation of sulfonium com-

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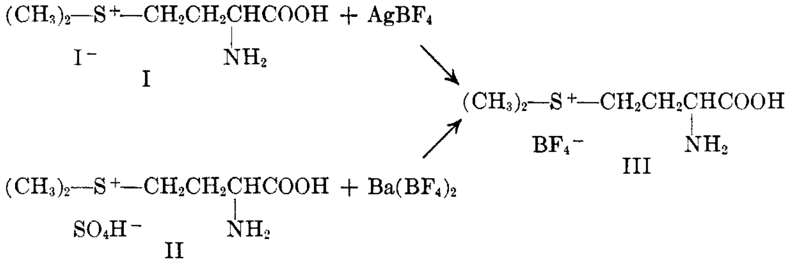
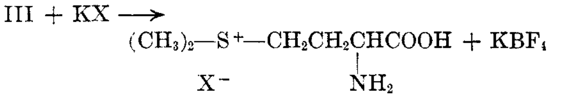
pounds,[6] it was found that sulfonium fluoborates were easily crystallized and relatively stable on storage. Methioninemethylsulfonium fluoborate (III) was prepared by the reaction of methioninemethylsulfonium iodide (I) with silver fluoborate, or by the reaction of methioninemethylsulfonium sulfate (II) with barium fluoborate.



$$\underset{\text{I}}{(CH_3)_2{-}\underset{I^-}{S^+}{-}CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCOOH} + AgBF_4 \searrow$$

$$\underset{\text{II}}{(CH_3)_2{-}\underset{SO_4H^-}{S^+}{-}CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCOOH} + Ba(BF_4)_2 \nearrow \underset{\text{III}}{(CH_3)_2{-}\underset{BF_4^-}{S^+}{-}CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCOOH} \quad (1)$$

Anion exchange Reaction 2 of III with potassium salts, KX, of various acids can be carried out smoothly in water or aqueous ethanol, and the sulfonium salts formed are separated effectively from the reaction mixture and recrystallized from suitable solvents to afford the corresponding sulfonium salts in good yields. Sulfonium salts thus



$$\text{III} + KX \longrightarrow (CH_3)_2{-}\underset{X^-}{S^+}{-}CH_2CH_2\underset{NH_2}{\underset{|}{C}}HCOOH + KBF_4 \quad (2)$$

prepared are shown in Table I.

An attempt to prepare methioninemethylsulfonium permanganate was unsuccessful. The sulfonium bromate (VII) is highly explosive and heat or shock must be avoided. Methioninemethylsulfonium salts of complex anions containing metals do not melt but at increased temperature undergo slow decomposition as indicated by a change in color. The sulfonium chromate (XII) turns from yellowish brown to dark brown above 125°, sulfonium bichromate (XIII) from orange to brown above 105°, sulfonium ferrocyanide (XIV) turns from light yellow to cream color above 125°, and sulfonium ferricyanide (XV) from yellow to greenish yellow above 115°. The sulfonium fluosilicate (XVII) and perchlorate (IX) cannot be prepared from III and the corresponding potassium salts; however, these compounds can conveniently be prepared by the reaction of I and silver fluosilicate or perchlorate. The former (XVII) is somewhat difficult to purify because of its very hygroscopic property, while the latter (IX), though not so hygroscopic as XVII, is less stable to heating than III. Methyl bromide,[1,2] ethyl bromide,[2] benzyl and *p*-methylbenzyl chlorides,[10] as well as *bis*(2-chloroethyl)sulfide[11] react directly with methionine to yield the corresponding sulfonium salts, but methyl and ethyl chlorides do not give sulfonium salts of methionine even at 60° in an autoclave, and the methionine may be recovered.[6]

EXPERIMENTAL[12]

Methioninemethylsulfonium iodide (I). A.[13] A mixture of 149 g. (1 mole) of methionine, 900 ml. of 80% formic acid, 380 ml. of acetic acid, and 225 ml. (3.6 moles) of methyl iodide was kept in a dark place at room temperature for 2 days. The solution was concentrated under diminished pressure below 60°. To the resulting sirupy material was added 1.5 l. of methanol, and the mixture was maintained at 0° overnight. The precipitate was filtered, and washed with methanol and acetone. Recrystallization from water-methanol-acetone gave 262 g. (90%) of I, colorless plates, melting at 156–157° dec. (reported[1] 150°).

B.[3] A mixture of 29.8 g. (0.2 mole) of methionine, 500 ml. of acetic acid, 50 ml. of water, and 75 ml. (1.2 moles) of methyl iodide was gently refluxed on a water bath for 1.5 hr. The mixture was treated similarly as above to yield 54 g. (92%) of I, melting at 156–157° dec.

Methioninemethylsulfonium fluoborate. A. To a solution of 29.1 g. (0.1 mole) of I in 280 ml. of water was added 35 g. of 56% aqueous silver fluoborate solution at room temperature with stirring until the iodine ion just disappeared (by means of a spot test using bismuth nitrate and 8-hydroxyquinoline.[14]) The mixture was filtered, and the filtrate was concentrated under diminished pressure below 50°. The residual sirup was treated as in the case of I. After recrystallization from aqueous methanol, 24.9 g. (95%) of III, colorless crystals, m.p. 147–148° dec., was obtained.

B. A solution of 14.9 g. (0.1 mole) of methionine in 100 ml. of 18*N* sulfuric acid and 6 ml. (0.14 mole) of methanol was refluxed for 3 hr. The mixture was diluted with 250 ml. of water and partly neutralized with powdered barium hy-

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(10) Benzyl and *p*-methylbenzyl chlorides reacted with methionine at 50–60° in 70% acetic acid.[8] Methioninebenzylsulfonium chloride had m.p. 123–124° dec. (Cl, calcd.: 12.9; found: 12.5), and methionine-*p*-methylbenzylsulfonium chloride, m.p. 131–132° (Cl, calcd.. 12.1; found: 11.8). Toennies and Kolbe reported[1b] that *N*-acetylmethionine reacted with cinnamyl chloride to yield corresponding sulfonium salt.

(11) W. H. Stein and S. Moore [*J. Org. Chem.*, **11**, 681 (1946)] reported the formation of this sulfonium salt which was, however, not crystallizable.

(12) All melting points are uncorrected.

(13) Method A is a modification of Toennies and Kolbe (reported 75% yield; see Ref. 1).

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TABLE I

DL-Methioninemethylsulfonium Salts

$(CH_3)_2S^+(X^-)CH_2CH_2CH(NH_2)COOH$

Number	Formula of Anion (X)^a	Method of Preparation^b	Dec. Pt., °C.	Analyses, % Nitrogen Calcd.	Nitrogen Found	Anion (X) Calcd.	Anion (X) Found
I	I	A	156–157^c	4.81	4.64	43.59	43.5
I	I	B	156–157	4.81	4.78	43.59	43.5
III	BF_4	C	147–148	5.58	5.51	34.58	34.5
III	BF_4	D	147–148	5.58	5.50	34.58	34.5
IV	Cl	B	137–138^d	7.01	6.90	17.76	17.7
IV	Cl	E	137–138	7.01	6.90	17.76	17.4
IV	Cl	F	137–138	7.01	6.90	17.76	17.9
V	Br	B	140–141^e	5.74	5.70	32.73	32.8
VI	ClO_3	B	129–130	—	—	39.69	40.1
VII	BrO_3	B	^{f}	—	—	43.78	44.9
VIII	IO_3	B	110–111	—	—	51.58	51.7
IX	ClO_4	G	147–148	—	—	37.71	36.1
X	NO_2	B	128–129	13.32	13.00	21.88	21.8
XI	NO_3	B	147–148	12.38	12.08	27.40	27.4
XII	$^1/_2CrO_4$	B	^{g}	6.30	6.11	26.10	26.0
XIII	$^1/_2Cr_2O_7$	B	^{g}	5.15	5.18	39.67	39.6
XIV	$^1/_4Fe(CN)_6$	B	^{g}	16.12	16.08	24.39	24.3
XV	$^1/_3Fe(CN)_6$	B	^{g}	17.89	17.65	30.08	30.0
XVI	NH_2SO_3	B	124–125	10.76	10.72	—	—
XVII	$^1/_2SiF_6$	H	109–110	5.95	5.81	30.19	30.0
XVIII	CH_2FCOO^{h}	B	121–122	5.81	5.86	—	—
XIX	CF_3COO	B	126–127	5.05	4.95	—	—
XX	$CHCl_2COO$	B	119–120	4.79	4.87	—	—
XXI	CCl_3COO	B	108–109	4.29	4.26	—	—
XXII	p-$NO_2C_6H_4COO$	B	147–148	7.65	7.90	—	—
XXIII	3,5-$(NO_2)_2C_6H_3COO$	B	141–142	11.19	11.28	—	—
XXIV	p-$CH_3C_6H_4SO_3$	B	143–144	4.18	4.08	—	—
XXV	β-$C_{10}H_7SO_3$	B	128–129	3.77	3.86	—	—
XXVI	p-$NH_2C_6H_4SO_3$	B	124–125	8.33	8.30	—	—
XXVII	4-$(CH_3)_2NC_6H_4N_2$-$C_6H_4SO_3$-4′	B	203–204	11.96	12.12	—	—

[a] All yields are from about 80 to 96%. [b] Method: A, Methionine with methyl iodide; B, III with potassium salt; C, I with silver fluoborate; D, Sulfonium sulfate (II) with barium fluoborate; E, I with silver chloride; F, IX with potassium chloride; G, I with silver perchlorate; H, I with silver fluoborate. [c] G. Toennies and J. J. Kolbe[1b] reported m.p. 150° dec.; M. Stahmann, J. S. Fruton, and M. Bergmann,[7] m.p. 168–169° dec.; F. Challenger and Y. C. Lin,[9] m.p. 157–158° dec.; R. O. Atkinson and F. Poppelsdorf,[2] m.p. 150° dec.; S. Nakajima and G. Okuyama,[4] m.p. 149° dec. [d] R. O. Atkinson and F. Poppelsdorf[2] reported m.p. 134° dec. [e] G. Toennies and J. J. Kolbe[1b] reported m.p. 140° dec.; W. Shive *et al.*,[8] m.p. 140° dec.; S. Nakajima and G. Okuyama,[4] m.p. 139° dec. [f] Several samples explosively decomposed in the range of 94–115° in spite of careful measurements of melting point. [g] This substance has no melting point. [h] This sulfonium salt is most likely a convulsant poison like other derivatives of fluoroacetic acid.

droxide to pH 2. The precipitated barium sulfate was filtered, and the filtrate was adjusted exactly to pH 5 with dilute barium hydroxide solution. The resulting mixture was filtered, and the filtrate[15] was treated with 15 g. of 30% aqueous barium fluoborate solution until no sulfate ion was detectable. Barium sulfate was again removed, and the clear filtrate was treated as above to yield 16.2 g. (67%) of III, melting at 147–148° dec.

Reaction of methioninemethylsulfonium fluoborate with potassium salts. To a solution of 0.05 mole of a potassium salt in 80 ml. of water was added with stirring a solution of 12.6 g. (0.05 mole) of III in 20 ml. of water. Ethanol (100 ml.) was then added to the above mixture. The potassium fluoborate formed was filtered, washed with 50% ethanol, and the filtrate was concentrated under diminished pressure below 50°. The residue was treated with 20 ml. of 70% ethanol, and the insoluble matter was removed by filtration. The filtrate was mixed with 200 ml. of methanol, and then acetone was added until the solution became turbid. The resulting mixture was maintained at 0° overnight to settle the precipitate. The precipitate was filtered, washed with methanol, and dried *in vacuo* to give a crude sulfonium salt. The crude product was recrystallized from water-methanol-acetone in suitable proportions to afford the pure sample listed in Table I.

Methioninemethylsulfonium perchlorate (IX). To a solution of 29 g. (0.1 mole) of I in 200 ml. of water was added a solution of 20.7 g. (0.1 mole) of silver perchlorate in 200 ml. of water. The mixture was treated as in the case of the preparation A of III to give 24.3 g. (92%) of IX which, after recrystallization from water-methanol, melted at 147–148° dec.

Methioninemethylsulfonium chloride (IV). A. IV was prepared in 91% yield through Reaction 2 of III and potassium chloride, and the product melted at 137–138° dec.

B. To a solution of 3.7 g. (0.05 mole) of potassium chloride in 60 ml. of water was added a solution of 12.6 g. (0.05 mole) of IX in 30 ml. of water. After cooling to 0°, the precipitated potassium perchlorate was filtered, and the filtrate was treated as described above to give 9.4 g. (94%) of IV, m.p. 137–138° dec.

C. To a suspension of 36 g. (0.25 mole) of freshly prepared

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(15) The filtrate contains sulfonium sulfate (II) which cannot be isolated as pure crystalline material because it is extremely hyrgoscopic.

silver chloride in 150 ml. of water was added dropwise with vigorous stirring a solution of 29 g. (0.1 mole) of I in 60 ml. of water. The addition required about 30 min. The mixture was stirred for an additional 2 hr. until no iodide ion was detected by a spot test.[14] The resulting mixture was filtered, and the filtrate was concentrated under diminished pressure to about 45 ml. The residue was treated as above to yield 17.6 g. (88%) of IV, which melted at 137–138° dec.

Methioninemethylsulfonium fluosilicate (XVII). To a solution of 29.1 g. (0.1 mole) of I in 50 ml. of water was added 37 g. of freshly prepared 48% aqueous silver fluosilicate solution, and the mixture was treated as above to yield 21.4 g. (91%) of XVII as hygroscopic colorless needles, m.p. 109–110° dec. XVII was found to decompose slowly *in vacuo* at room temperature. XVII could be converted in good yield into IV by a procedure similar to that for XI.

KYOTO, JAPAN

[CONTRIBUTION FROM THE MATERIALS & PROCESSES STAFF, AERO-SPACE DIVISION, BOEING AIRPLANE COMPANY]

Synthesis of Monomeric Silanes

ALLEN E. SENEAR, JOSEPH WIRTH, AND ROY G. NEVILLE[1]

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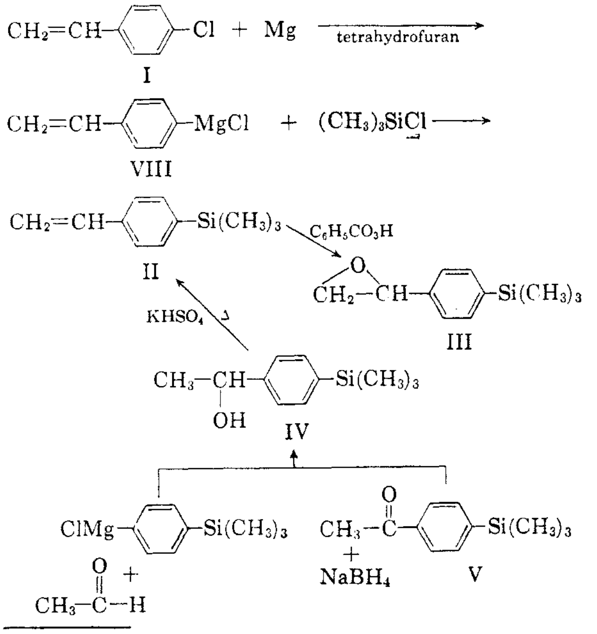
The preparations of 4-trimethylsilylstyrene and of 4-epoxyethylphenyltrimethylsilane are described, as well as attempts to extend these reactions to the preparation of the analogous difunctional monomers.

Two methods for the preparation of 4-trimethylsilylstyrene (II) have recently been described. Winslow[2] prepared it by the vapor phase dehydration of 1′-(4-trimethylsilylphenyl)ethanol (IV). Later Lewis[3] described the reaction of 4-styryltrichlorosilane with methylmagnesium bromide. In the present report, the synthesis of II from 4-styrylmagnesium chloride (VIII)[4] and trimethylchlorosilane is described. The conversion of the styrylsilane (II) to the corresponding epoxide (III) is also included. In addition, details are given for the preparation of Winslow's alcohol (IV) in crystalline form by the reduction of 4-trimethylsilylacetophenone[5,6] as well as from *p*-dichlorobenzene instead of the more expensive *p*-dibromo compound.



A number of attempts were made to prepare the analogous difunctional compounds, di(4-styryl)dimethylsilane and di(4-epoxyethyl)dimethylsilane. Reaction of 4-styrylmagnesium chloride (VIII) with dimethyldichlorosilane appears to proceed normally, but attempts to isolate the product invariably led to polymer formation.

Reduction of di(4-acetylphenyl)dimethylsilane to the dialcohol, followed by dehydration, was next attempted. Although the reduction proceeded smoothly, attempts to dehydrate the dialcohol led to splitting of the silicon-phenyl bond.

In a previous paper from this laboratory, the use of 2-(4′-bromophenyl)-2-methyl-1,3-dioxolane as a reagent for the introduction of the 4-acetylphenyl group into silanes was described.[6] During the present work, we have discovered that the 1,3-dioxolane (ketal) structure is more stable than anticipated. Depending on the method of working up the Grignard product, it is possible to isolate pure ketals, pure ketones, or mixtures of these compounds. When water is used to decompose the Grignard product from trimethylchlorosilane, a ketal can be isolated. Treatment of this Grignard product with dilute hydrochloric acid in the cold yields a mixture of ketal and ketone. Use of hydrochloric acid plus gentle heat yields the ketone. Treatment of the difunctional Grignard product derived from dimethyldichlorosilane with water to yield the diketal proceeds smoothly. Acid treatment of this Grignard product, designed to split the ketal groups, yields a mixture of ketal, ketone, and decomposition products which is difficult to purify. After purifica-

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(1) Present address: Propulsion Dept., Missile and Space Division, Lockheed Aircraft Corp., Palo Alto, Calif.

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