precipitated was filtered and recrystallized from benzene to give *di-(4-methoxy-1-naphthyl)methane* (III), m.p. 150.5–152.0°.

Anal. Calc'd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.17. Found: C, 83.76; H, 6.07.

Oxidation of III. A solution of III (2.5 g.) in glacial acetic acid (75 ml.) was heated to reflux, and a solution of sodium dichromate (5 g.) in acetic acid was added slowly; the mixture was refluxed for two hours, cooled, and poured into ice-water, yielding *di-(4-methoxy-1-naphthyl)ketone,* m.p. 143–144° after recrystallization from methanol.

Anal. Calc'd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.29. Found: C, 80.67; H, 5.31.

The Cannizzaro reaction of I was carried out under the following conditions: (a) The aldehyde was treated with 66% potassium hydroxide at room temperature and allowed to stand for 24 hours.[3] (b) A mixture of aldehyde (9 g.) and potassium hydroxide (7 g.) in water (5 ml.) was stirred at room temperature for 24 hours.[2] (c) The reaction mixture, containing the same proportions of starting materials as b, was heated on a steam-bath for 12 hours. From both (a) and (b) only starting material could be recovered, while from (c) only 4-methoxy-1-naphthoic acid (3 g.) could be isolated. There was no evidence of 4-methoxy-1-naphthalenemethanol.

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Addition of Mercaptans to Vinyl Silanes

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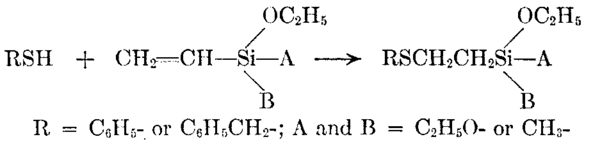
In an effort to prepare polar organosilicon monomers containing β-sulfone side groups, the addition of thiophenol and benzyl mercaptan to vinyl silanes containing ethoxy groups has been carried out.

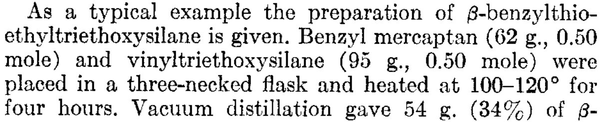


$$RSH + CH_2{=}CH{-}\overset{OC_2H_5}{\underset{B}{Si}}{-}A \longrightarrow RSCH_2CH_2\overset{OC_2H_5}{\underset{B}{Si}}{-}A$$

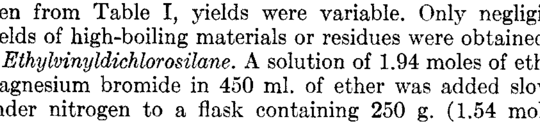
R = C_6H_5- or $C_6H_5CH_2$-; A and B = C_2H_5O- or CH_3-

Burkhard[1] has previously reported the addition of mercaptans to allyltrimethylsilane and allyltriethoxysilane. The β sulfide isomer is assumed based on the work of Burkhard and the expected addition of an RS· radical on steric and resonance grounds[2] to the least hindered carbon to give the most resonance-stabilized radical.

The vinylmethyl- and vinyldimethyl-ethoxysilanes used in the present work were prepared by treatment of vinyltriethoxysilane with methylmagnesium iodide.[3] During this investigation the hitherto unreported ethylvinyldichlorosilane and ethylvinyldiethoxysilane have been prepared according to the equations given below



$$CH_2{=}CHSiCl_3 + C_2H_5MgBr \longrightarrow CH_2{=}CH\overset{C_2H_5}{Si}Cl_2 + MgBrCl$$



EXPERIMENTAL

Addition of mercaptans to vinylethoxysilanes. Mercaptans and olefins in a 1:1 ratio were heated together at 80–130° for four to eight hours. The reactants were miscible, and the products were recovered by distillation. Yields were not appreciably improved by increasing the reaction time to 48 hours or by adding a large excess of mercaptan.

As a typical example the preparation of β-benzylthioethyltriethoxysilane is given. Benzyl mercaptan (62 g., 0.50 mole) and vinyltriethoxysilane (95 g., 0.50 mole) were placed in a three-necked flask and heated at 100–120° for four hours. Vacuum distillation gave 54 g. (34%) of β-benzylthioethyltriethoxysilane (Table I). Initial fractions represented impure starting materials in most cases. As seen from Table I, yields were variable. Only negligible yields of high-boiling materials or residues were obtained.

Ethylvinyldichlorosilane. A solution of 1.94 moles of ethylmagnesium bromide in 450 ml. of ether was added slowly under nitrogen to a flask containing 250 g. (1.54 moles) of vinyltrichlorosilane in 250 ml. of ether held at 10–20°. After filtration the liquid phase was fractionated through a vacuum-jacketed column packed with glass helices to give 94 g. (40%) of ethylvinyldichlorosilane, b.p. 122–124°.

Anal. Calc'd for $C_4H_8Cl_2Si$: C, 30.97; H, 5.16; Neut. equiv., 77.7.[4] Found: C, 31.09; H, 5.19; Neut. equiv., 77.9.

Ethylvinyldiethoxysilane. This compound was prepared essentially according to the procedure of Sauer.[5] From 0.258 mole of ethylvinyldichlorosilane, 0.57 mole of pyridine, and 1.03 moles of absolute ethanol, there was obtained 13 g. (29%) of ethylvinyldiethoxysilane, b.p. 48.5–51.5° at 12–13 mm.

Anal. Calc'd for $C_8H_{18}O_2Si$: C, 55.12; H, 10.41. Found: C, 55.30; H, 10.41.

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[3] Cohen and Ladd, *J. Am. Chem. Soc.*, **75**, 988 (1953).

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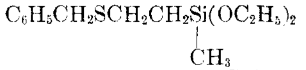
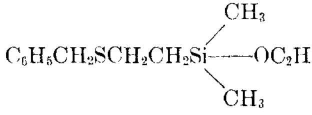
[5] Sauer, *J. Am. Chem. Soc.*, **66**, 1709 (1944).

TABLE I

PREPARATION OF NEW SILANE SULFIDES

Formula	Reaction Conditions				Yield, %	Analysis					
	Temp.	Hours	B.p., °C.	Mm.		Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found	Sulfur Calc'd	Sulfur Found
$C_6H_5SCH_2CH_2Si(OC_2H_5)_3$	80–100	6	130	0.8	75	55.96	56.07	8.05	8.19	10.67	10.46
$C_6H_5CH_2SCH_2CH_2Si(OC_2H_5)_3$	100–120	4	125–126	0.3–0.4	34	57.28	57.19	8.33	8.40	10.20	10.34
 $C_6H_5CH_2SCH_2CH_2Si(CH_3)(OC_2H_5)_2$	110–130	8	114	0.2	36	59.15	59.41	8.45	8.33	11.27	11.18
 $C_6H_5CH_2SCH_2CH_2Si(CH_3)_2OC_2H_5$	125–130	10	107	0.5	26	61.42	61.60	8.66	8.60	12.60	12.41

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The Electrolysis of (+)-2-Methylbutanoic Acid[1a]

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It has long been suspected that the Kolbe electrolysis of carboxylic acids and the decomposition of diacyl peroxides proceed by way of a common intermediate.[2–4] This hypothesis has been reinforced by the similarity of the products isolated in both reactions.[3,4] In addition the nature of the products has suggested free radical mechanisms for both reactions.[3–7] The isolation of optically active hydrocarbon,[8] alcohol[8] and ester[8,9] of retained configuration from the decomposition of optically active diacyl peroxides has led us to inquire into the stereochemical nature of the products of the electrolysis of an optically acid. We now report the results of such an investigation.

Electrolysis of (+)-2-methylbutanoic acid gave, directly, inactive 2-butanol, identified as the α-naphthylurethan, and the (±)-2-butyl ester of (+)-2-methylbutanoic acid, identified by comparison with a synthetic product and by saponification to inactive 2-butanol and optically active (+)-2-methylbutanoic acid.

Since Wallis and Adams have reported[10] the isolation of inactive 2,3-dimethylhexane from the electrolysis of (+)-2-methylbutanoic acid, it can now be concluded that the products of the Kolbe electrolysis of carboxylic acids and those of the decomposition of diacyl peroxides, although chemically similar, are formed by stereochemically different paths. In explanation of this discrepancy, the view may be taken that radicals are formed in both reactions but that their subsequent fate is a function of the particular mode of generation and the environment into which they are produced. Alternatively, it is to be noted that in the case of the decomposition of diacyl peroxides, recombination of radicals within the solvent cage or internal rearrangement *via* cyclic transition states[8] are possibilities which appear rather less likely in the course of the electrolysis reaction.

EXPERIMENTAL

(+)-2-Methylbutanoic acid. The acid, α^{27}_{D} +17.85° (*l*, 1, neat), was prepared in 70% yield by permanganate oxidation[11] of 99% optically pure (−)-2-methyl-1-butanol, α^{20}_{D} −4.80° (*l*, 1, neat), obtained by fractionation of commercial fusel oil[12] through a Podbielniak Hyper-Cal column.

Electrolysis of (+)-2-methylbutanoic acid. The cathode consisted of a perforated platinum foil cylinder, 1.3 cm. in diameter and 5 cm. high, mounted on a stout platinum wire; the anode was a platinum wire 0.038 cm. in diameter with a surface area of 2.26 cm.[2] The current during the

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(1a) Presented at the Meeting-in-miniature, New York A. C. S. Section, March 16, 1956.

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