centrated sulfuric acid, and 250 ml. of water was refluxed for 2 hours. The dark-red solution was decanted from a black tar and the solution was cooled to room temperature. The brown solid which precipitated on cooling was filtered and air-dried. The solid was suspended in 250 ml. of ether, filtered, and the wash treatment repeated. To a beaker containing the washed amine sulfate there then was added a saturated solution of sodium bicarbonate until excess bicarbonate was present (no more evolution of gas). The solid remaining was filtered, washed with a small portion of water, and air-dried, giving 25 g. (31.4 percent) of 2-amino-5-nitroethylbenzene, m.p. 87°.

Attempted distillation of the decanted tar lead to its violent decomposition as described above.

2,5-Diaminoethylbenzene. A solution of 206 g. of 2-amino-5-nitroethylbenzene (IV), in 1600 ml. of absolute ethanol distilled from Raney nickel, was reduced in 400-ml. batches, with platinum oxide and hydrogen at room temperature and 30–50 p.s.i. The ethanol was removed under nitrogen and reduced pressure, and the resulting deep-red solution was distilled at 9 mm. pressure, (b.p. 141–144°) to give 150 g. (88.8%) of a light-yellow liquid which solidified on cooling.

Anal. Calc'd for $C_8H_{12}N_2$: C, 70.56; H, 8.88; N, 20.56. Found:[2] C, 70.6; H, 8.9; N, 20.3.

The diamine is very sensitive to air and quickly turns black on standing. This sensitivity is probably an oxidative phenomenon facilitated by the *para* relationship of the amino groups. Metals appear to catalyze the decomposition. A crude melting point gave a value of about 33°. The diacetylamino derivative was prepared by mixing 1 g. of the diamine and 20 ml. of acetic anhydride at room temperature. After shaking for one minute, the mixture was poured into water and the suspension was filtered. Two crystallizations from ethanol-water gave colorless needles, m.p. 219°.

Anal. Calc'd for $C_{12}H_{16}N_2O_2$: C, 65.50; H, 7.27. Found:[2] C, 65.5; H, 7.4.

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4-Methoxy-1-naphthalenemethanol

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In connection with our research 4-methoxy-1-naphthalenemethanol was desired. This compound had been described by Madinaveitia and Puyal[2] as a solid, m.p. 35°, obtained from the Cannizzaro reaction of 4-methoxy-1-naphthaldehyde (I). Careful repetition of this procedure as well as of the modified procedure given by Shoesmith and Rubli[3] yielded only unreacted I. Under more vigorous conditions 4-methoxy-1-naphthoic acid was obtained, but no carbinol could be isolated.

Reduction of I with lithium aluminum hydride gave a solid (II), m.p. 76–77°, from which an acetate and a phenylurethan could be prepared. These compounds all gave analyses agreeing with the theory for a methoxy-naphthalenemethanol and its derivatives. Oxidation of II with alkaline potassium permanganate gave an acid which did not depress the melting point of authentic 4-methoxy-1-naphthoic acid. The method of preparation, the analyses and the oxidation experiment indicates that II is 4-methoxy-1-naphthalenemethanol. Therefore the compound described by Madinaveitia,[2] for which he reported no analyses, is not the carbinol, and from our work as well as from the m.p., which is identical with that of I, it appears that their product was unreacted I. The reported phenylurethan, for which the author likewise gave no analysis (m.p. 240°),[2] might have been diphenylurea (m.p. 240°).

Attempts were made to obtain II directly from 1-methoxynaphthalene by hydroxymethylation with paraformaldehyde in acidic medium. However, only di-(4-methoxy-1-naphthyl)methane (III) was obtained, oxidation of which gave the corresponding dinaphthyl ketone.

EXPERIMENTAL[4]

Reduction of 4-methoxy-1-naphthaldehyde (I). Compound I, prepared by the procedure of Brady and Goldstein,[5] was reduced with lithium aluminum hydride in ether solution in the usual manner[6] to give *4-methoxy-1-naphthalenemethanol* (II), m.p. 76–77° after recrystallization from ether-petroleum ether.

Anal. Calc'd for $C_{12}H_{12}O_2$: C, 76.58; H, 6.43. Found: C, 76.22; H, 6.35.

The *acetate*, m.p. 63–64° after recrystallization from aqueous methanol, was prepared by refluxing II with acetic anhydride.

Anal. Calc'd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.12. Found: C, 72.99; H, 6.35.

The *phenylurethan*, m. p. 103–105°, was prepared in the usual manner.

Anal. Calc'd for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.57. Found: C, 74.50; H, 5.46.

Oxidation of II with alkaline potassium permanganate gave *4-methoxy-1-naphthoic acid*, m.p. 233° (reported, 234°),[7] the mixture melting point of which with an authentic sample showed no depression.

Reaction of 1-methoxynaphthalene with paraformaldehyde. Paraformaldehyde (9 g., 0.3 mole) and 30% sulfuric acid (50 ml.) were stirred with 1-methoxynaphthalene (40 g., 0.25 mole) overnight. The white solid (20 g., 40%) which

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[2] A. Madinaveitia and J. Puyal, *Anales real soc. espan. fis. quim.*, **17**, 125 (1919).

[3] J. Shoesmith and H. Rubli, *J. Chem. Soc.*, 3098 (1927).

[4] All melting points are uncorrected.

[5] O. L. Brady and R. Goldstein, *J. Chem. Soc.*, 1962 (1927).

[6] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

[7] L. Ruzicka, *Helv. Chim. Acta*, **15**, 907 (1932).

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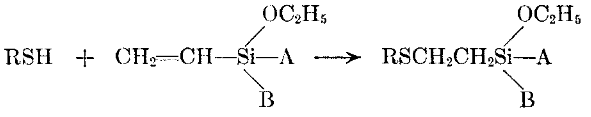
In an effort to prepare polar organosilicon monomers containing β-sulfone side groups, the addition of thiophenol and benzyl mercaptan to vinyl silanes containing ethoxy groups has been carried out.

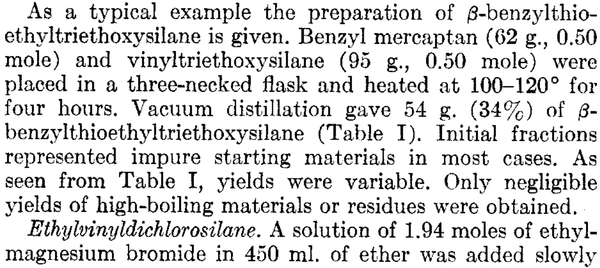


$$\mathrm{RSH} + \mathrm{CH_2{=}CH{-}}\underset{\mathrm{B}}{\overset{\mathrm{OC_2H_5}}{\mathrm{Si}}}\mathrm{{-}A} \longrightarrow \mathrm{RSCH_2CH_2}\underset{\mathrm{B}}{\overset{\mathrm{OC_2H_5}}{\mathrm{Si}}}\mathrm{{-}A}$$

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



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

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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