Analyses for silicon and chlorine were complicated by the extreme sensitivity of the products to oxygen and moisture. Micropipets and other conventional apparatus could not be used because the adsorbed water on the glass caused immediate hydrolysis. Recourse was had to constricted sample tubes 6 × 60 mm. which were heated to 500°, cooled in a dry-box filled with nitrogen, filled with the samples from a drawn-out capillary (which also had been cooled in the dry-box), and then stoppered and sealed. To analyze for silicon the weighed tubes were broken in the middle and dropped into 5 ml. of absolute alcohol (in which all products were very soluble), and several drops of dilute ammonia water added. The solutions were boiled for one hour, and the resulting silica was filtered, dried and weighed in the usual manner, the empty sample tubes being reweighed afterward. To analyze for chlorine, the weighed sample tubes were broken into a known volume of standardized solution of sodium hydroxide in alcohol, and the excess base titrated against standard acid. After the titration was finished, the empty sample tubes were rinsed with dilute hydrofluoric acid to remove the adhering silica and then were weighed back. The results are given in Table I.

TABLE I

Fraction	Boiling range at 1 mm., °C.	Properties	Si, %	Cl, %
2	70–120	Colorless light oil	20.88 20.86	80.2
3	120–170	Viscous oil	23.2	67.5 66.8
4	170–200	Very viscous yellow oil	23.9	79.0

Fractions 2 and 3 appear to be composed of familiar chlorinated di-, tri-, and tetrasilanes and siloxanes, as reported by Troost and Hautefeuille.[1] However, fraction 4 appears to be identical with the "subchloride" of silicon richest in chlorine obtained by Hertwig and Wiberg[4] from the reduction of silicon tetrachloride with hydrogen in an electric discharge. On the basis of the silicon contents, their substance had the empirical composition $SiCl_{2.6}$ and ours $SiCl_{2.61}$.

The publication by Hertwig and Wiberg[4] appeared while this investigation was in progress, and since Hertwig showed at once that their subchloride would absorb methyl chloride to produce methylchlorosilanes,[7] it seemed unnecessary to continue our work. We have shown that under appropriate conditions silicon tetrachloride can be reduced by silicon to form a lower chloride similar to that produced by reduction with hydrogen in an electric discharge.

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[7] K. A. Hertwig, *Z. Naturforsch.*, **6b**, 337 (1951).

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Formylation of the Dimethoxybenzenes Using Phosphorus Oxychloride and N-Methylformanilide

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An indication[1] in the literature that formylation of 1,3-dimethoxybenzene with phosphorus oxychloride and N-methylformanilide gives 2,6-dimethoxybenzaldehyde instead of the expected 2,4-dimethoxybenzaldehyde prompted an investigation of this reaction. The same reagents were combined with veratrole and 1,4-dimethoxybenzene for comparative purposes.

Treatment of 1,3-dimethoxybenzene with phosphorus oxychloride and N-methylformanilide mixture by a procedure described earlier[2] gave an 85% yield of 2,4-dimethoxybenzaldehyde. More vigorous conditions were required to convert veratrole and 1,4-dimethoxybenzene to veratraldehyde and 2,5-dimethoxybenzaldehyde, and the yields were lower than with the meta isomer. Veratraldehyde has been synthesized[3] by the analogous reaction of veratrole with formylpiperidine and phosphorus oxychloride in a yield comparable to that reported here. However, condensation of 1,3-dimethoxybenzene with a mixture of formyldiethylamine and phosphorus trichloride yielded only 40% of 2,4-dimethoxybenzaldehyde. The following procedure appears to be superior to previously described methods for synthesizing this aldehyde.

Experimental

2,4-Dimethoxybenzaldehyde.—Equimolar quantities of phosphorus oxychloride (153 g., 1 mole) of N-methylformanilide (135 g., 1 mole) were placed in a 1-l., 3-neck flask and allowed to stand for 45 minutes. To this mixture was added, during 70 minutes with stirring, 138 g. (1 mole) of 1,3-dimethoxybenzene while the internal temperature was held at 25° by a cold water-bath. When addition was complete the bath was removed and the mixture was stirred for 3 hours longer during which time the temperature rose to 34°. The sirupy red mixture was allowed to stand overnight and was then poured slowly with good stirring into 2.5 l. of cold water. The resulting solid was collected and washed well with water on the filter. The wet cake was dissolved in 250 ml. of warm benzene, and the aqueous layer was separated and shaken with 50 ml. of benzene. The combined extracts were concentrated and distilled from a Claisen flask, yielding 141 g. (85%) of aldehyde, b.p. 110° (0.1 mm.), m.p. 68–70°. The **oxime** melts at 105–106° (lit.[4] 106°). The **semicarbazone**, from alcohol, melts at 203°.

Anal. Calcd. for $C_{10}H_{13}N_3O_3$: N, 18.82. Found: N, 18.78.

Veratraldehyde.—Veratrole (27.6 g., 0.2 mole) was added to an equimolar amount of the formylating mixture prepared as described above and the mixture was stirred at 70° for 18 hours. It was poured into water and ice and the product extracted with ether. The extract was shaken with sodium bicarbonate solution, dried and distilled. This gave 15.3 g. of product, b.p. 167–170° (21 mm.), m.p. 39–42°. It was recrystallized from cyclohexane and 12.5 g. (38%) of aldehyde, m.p. 44–45°, was obtained.

2,5-Dimethoxybenzaldehyde.—By the procedure described for veratraldehyde there was obtained a 16% yield of this aldehyde, m.p. 51°. The ***p*-nitrophenylhydrazone** melts at 216°.[5]

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[1] L. N. Ferguson, *Chem. Revs.*, **38**, 231 (1946).

[2] A. W. Weston and R. J. Michaels, Jr., *Org. Syntheses*, **31**, 108 (1951).

[3] S. Akabori and Y. Senoh, *Bull. Chem. Soc. Japan*, **14**, 166 (1939); *C. A.*, **33**, 6270 (1939).

[4] L. Gattermann, *Ann.*, **357**, 369 (1907).

[5] H. H. Hodgson and H. G. Beard, *J. Chem. Soc.*, 2339 (1927).

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NEW COMPOUNDS

Dimercaptols of Acetonylacetone

The *n*-tetradecyl- and *n*-octadecyl dimercaptols of acetonylacetone were prepared in approximately 60% yield by the procedure described by Rietz, Chapman and Fernandez.[1]

The tetradecyl derivative, m.p. 73°, was purified by crystallization from ethyl ether. *Anal.* Calcd. for $C_{62}H_{126}S_4$. C, 74.47; H, 12.71; S, 12.81. Found: C, 74.37; H, 12.69; S, 12.66.

The octadecyl derivative, m.p. 82°, was purified by crystallization from isopropyl ether. *Anal.* Calcd. for $C_{78}H_{158}S_4$: C, 76.52; H, 13.00; S, 10.49. Found: C, 76.53; H, 12.83; S, 10.59.

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(1) Rietz, Chapman and Fernandez, THIS JOURNAL, **70**, 3486 (1948).

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2,2-Dimethyl-5-dimethylammonium-1,3-benzodioxole Iodide and 2,2-Dimethyl-5-trimethylammonium-1,3-benzodioxole Iodide

A solution of 6.5 g. (0.033 mole) of 2,2-dimethyl-5-nitro-1,3-benzodioxole[1] in 200 ml. of absolute ethanol was hydrogenated in the presence of 1.5 g. of Raney nickel catalyst at 60° and 5 atmospheres of hydrogen for 3 hours. The resulting amine solution was separated from catalyst by filtration in an inert atmosphere, then evaporated under reduced pressure to half its volume, and mixed with 10 g. (0.07 mole) of methyl iodide. A precipitate which formed soon after addition of the methyl iodide was isolated after four days and washed with ethyl ether. The colorless precipitate was extracted with 30 ml. of hot chloroform, and the chloroform solution evaporated to dryness. The chloroform-insoluble fraction was recrystallized from absolute ethanol; yield 0.85 g., m.p. 264° (dec.). The chloroform-soluble fraction was purified in the same way; yield 1.5 g., m.p. 216° (dec.). The analysis of the higher-melting compound corresponded to that of 2,2-dimethyl-5-trimethylammonium-1,3-benzodioxole iodide. *Anal.* Calcd. for $C_{12}H_{18}NO_2I$: C, 43.0; H, 5.4; N, 4.2. Found: C, 42.8; H, 5.6; N, 3.9. The lower-melting compound gave an analysis corresponding to that calculated for 2,2-dimethyl-5-dimethylammonium-1,3-benzodioxole iodide. *Anal.* Calcd. for $C_{11}H_{16}NO_2I$: C, 41.1; H, 5.0; N, 4.4. Found: C, 41.3; H, 5.2; N, 4.1.

Additional amounts of both products were isolated from the alcoholic mother liquor of the reaction mixture by precipitation with ether.

Attempted conversion of the two compounds to the corresponding catechol polymethylammonium chlorides by treatment with a hot mixture of aqueous hydrochloric acid and silver chloride led to the isolation of glasses which could not be crystallized. These glasses, when made basic, were subject to air oxidation, which causes them to become highly colored.

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(1) G. Slooff, *Rec. trav. chim.*, **54**, 995 (1935).

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RECEIVED JULY 7, 1952

The γ-Lactone of 3-Tridecyl-4-hydroxy-2-butenoic Acid

1-Acetoxy-2-pentadecanone.—A 70% yield of a white waxy solid, b.p. 153–163° (2 mm.), m.p. 49–52°, was obtained by treating myristoyl chloride with diazomethane and the azide thus obtained with glacial acetic acid.

3-Tridecyl-4-hydroxy-2-butenoic Acid, γ-Lactone.—An anhydrous benzene–ether solution of 1-acetoxy-2-pentadecanone (14.0 g.) reacted with granular zinc (3.53 g.) and ethyl bromoacetate (7.35 g.). The zinc complex was hydrolyzed and the intermediate thus obtained was dehydrated and lactonized by a saturated solution of anhydrous hydrogen bromide in glacial acetic acid. An oil, b.p. 185–195° (3–4 mm.), was obtained and recrystallization from alcohol and water gave a white solid, m.p. 57–58°. The product gave a positive Legal test, a negative potassium ferricyanide test, a positive Tollens test and it did not add bromine. The Legal test became negative after treatment with alcoholic potassium hydroxide. The melting point of a mixture with myristic acid was lowered 5°.

Anal. Calcd. for $C_{17}H_{30}O_2$: C, 76.6; H, 11.4. Found: C, 75.6; H, 11.4.

1-Acetoxy-2-heptadecanone.—A 68% yield of a white waxy solid, m.p. 62–63°, was obtained from palmitoyl chloride as described above. The product gave a positive ketone test with 2,4-dinitrophenylhydrazine. The melting point of a mixture with palmitic acid was not depressed. Two attempts to prepare a lactone from this compound failed.

Anal. Calcd. for $C_{19}H_{36}O_3$: C, 73.0; H, 11.6. Found: C, 73.0; H, 11.6.

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α-(Benzylmercaptomethyl)-succinic Anhydride

Dimethyl α-(Benzylmercaptomethyl)-succinate.—A solution of 31.6 g. (0.2 mole) of dimethyl itaconate in 50 cc. of absolute ethanol was treated with 27.2 g. (0.22 mole) of benzylmercaptan after the addition of 5 drops of piperidine. The mixture was refluxed for 10 hr., then the solvent was removed and the residue heated at *ca.* 110–120° for two hours before fractionation. A 78% yield of golden oil, b.p. 153–160° (0.7–0.8 mm.) was obtained; redistillation gave pure dimethyl α-(benzylmercaptomethyl)-succinate, b.p. 154–156° (0.7 mm.), $n^{25}\mathrm{D}$ 1.5250.

Anal. Calcd. for $C_{14}H_{18}O_4S$: S, 11.35. Found: S, 11.30.

α-(Benzylmercaptomethyl)-succinic Acid.—A mixture of 30.5 g. (0.107 mole) of dimethyl α-(benzylmercaptomethyl)-succinate and a solution of 15.5 g. of 85% potassium hydroxide (0.235 mole) in 50 cc. of water was refluxed five hours. The solution was charcoaled, extracted with ether and the aqueous layer acidified, extracted with ether and dried. A creamy white solid (21.5 g., 79% yield) remained after the removal of solvent and cooling of the residue. The crude product (m.p. 104–106°) was crystallized twice from 3:2 hexane–benzene to yield the pure acid in the form of white blades, m.p. 108.5–109° (cor.).

Anal. Calcd. for $C_{12}H_{14}O_4S$: C, 56.67; H, 5.55; S, 12.61. Found: C, 56.49; H, 5.33; S, 12.65.

α-(Benzylmercaptomethyl)-succinic Anhydride.—There was refluxed 15.26 g. (0.6 mole) of α-(benzylmercaptomethyl)-succinic acid and 50 cc. of acetic anhydride for 4 hours, and then the excess acetic anhydride removed. The residue was distilled, and 11.8 g. (83% yield) of golden oil collected at 150–155° (0.2 mm.). The oil solidified after some standing and crystallized from benzene–cyclohexane as fine white needles, m.p. 58–58.5° (cor.).

Anal. Calcd. for $C_{12}H_{12}O_3S$: C, 61.00; H, 5.12; S, 13.57. Found: C, 60.70; H, 5.36; S, 13.32.

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Ethyl β-Benzylmercaptopropionate

A solution of 12.0 g. (0.52 mole) of sodium in 150 cc. of absolute ethanol was treated (reflux, stirring, 0.5 hr.) with 64.5 g. (0.52 mole) of benzylmercaptan at 30–40°, then refluxed for an hour. To the sodium benzylmercaptide was added (one hour) a solution of 90.5 g. (0.5 mole) of ethyl β-bromopropionate in 75 cc. of absolute ethanol and the mixture refluxed three hours. The mixture was quenched in considerable water, extracted with ether, then the extracts washed (saturated sodium chloride solution) and dried over sodium sulfate. Fractionation of the extract gave 92.7 g. (87.5% yield) of ethyl β-benzylmercaptopropionate; b.p. 101–103° (0.22 mm.), $n^{25}\mathrm{D}$ 1.5305.

Anal. Calcd. for $C_{11}H_{16}O_2S$: C, 62.23; H, 9.05; S, 15.10. Found:[1] C, 62.29; H, 9.37; S, 14.88.

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(1) Analyses by Mr. M. E. Auerbach and Miss P. Curran.