

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.<sup>1</sup> However, fraction 4 appears to be identical with the "subchloride" of silicon richest in chlorine obtained by Hertwig and Wiberg<sup>4</sup> 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<sub>2.6</sub> and ours SiCl<sub>2.61</sub>.

The publication by Hertwig and Wiberg<sup>4</sup> appeared while this investigation was in progress, and since Hertwig showed at once that their subchloride would absorb methyl chloride to produce methylchlorosilanes,<sup>7</sup> 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<sup>1</sup> 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

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

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<sup>2</sup> 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<sup>3</sup> 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 formyl-diethylamine 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.<sup>4</sup> 106°). The semicarbazone, from alcohol, melts at 203°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>: 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*-nitrophenylhydrazones melts at 216°.<sup>5</sup>

(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 Acetylacetone

The *n*-tetradecyl- and *n*-octadecyl dimercaptols of acetylacetone were prepared in approximately 60% yield by