and refluxed for 1.5 hours. The supernatant solution was decanted, and the residue, remaining after distillation of the solvent, was distilled *in vacuo*. There was obtained 6.8 g. (46%) of crystalline material, b.p. 126–153° (1–2 mm.), sufficiently pure for further work. Recrystallization from hexane afforded colorless crystals, m.p. 52–55°.

Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.53; H, 4.84. Found: C, 70.47; H, 4.85.

4-(2',3'-Dimethoxyphenyl)-5-carbethoxy-6-methyl-α-pyrone.—A solution of 2.4 g. of ethyl 2,3-dimethoxyphenylpropiolate and 2.0 g. of ethyl acetoacetate was treated with 0.25 g. of dry sodium ethoxide, and the mixture was heated on the steam-cone for 3.5 hours. After cooling, the mixture was taken up in cold water, and the neutral product was isolated as usual. Trituration with pentane gave 2.2 g. of crystals, m.p. 110–113°. Recrystallization from methanol led to colorless crystals, m.p. 114–116°.

Anal. Calcd. for $C_{17}H_{18}O_6$: C, 64.16; H, 5.70. Found: C, 63.94; H, 5.55.

The infrared spectrum (chloroform) had a peak at 5.8–5.85 μ.

Condensation of 3.2 g. of 2,3-dimethoxyphenylpropiolonitrile with 3.4 g. of ethyl acetoacetate in the presence of 0.4 g. of dry sodium ethoxide at 100° for 16 minutes afforded 0.5 g. of this α-pyrone and 3.5 g. of alkali-soluble, red oil. The latter material gave a purple color with ferric chloride and was gradually transformed to a tar upon exposure to air. It probably was an uncyclized addition product. Further treatment of the material with sodium ethoxide afforded additional pyrone, III.

An attempt to condense 2,3-dimethoxyphenylpropiolamide with ethyl acetoacetate in the presence of sodium ethoxide at 100° for 20 hours resulted in complete recovery of the amide.

Enol IIA.—A mixture of 10.5 g. of ethyl 2,3-dimethoxyphenylpropiolate, 7.0 g. of acetylacetone and 1.0 g. of dry sodium ethoxide was heated on the steam-cone for seven days. The reaction was quenched with cold water, and the aqueous solution was washed with ether. Acidification gave 4.8 g. of enol, m.p. 140–145°, after trituration with ether. Recrystallization from benzene gave colorless needles, m.p. 145.5–147°.

Anal. Calcd. for $C_{16}H_{18}O_6$: C, 62.74; H, 5.92. Found: C, 62.84; H, 5.85.

The compound gave a red-violet color with ferric chloride. The infrared spectrum (chloroform) had a band at 3.1–3.3 μ and a peak at 5.92 μ (bonded acid carbonyl).

Enol IIB.—A mixture of 3.4 g. of 2,3-dimethoxyphenylpropiolonitrile, 2.7 g. of acetylacetone and 0.35 g. of dry sodium ethoxide was heated at 100° for three hours. The mixture was treated with cold water, and the aqueous solution was washed with ether and acidified at ice temperature. The product was extracted with ether. The ether solution was dried over magnesium sulfate, and the ether was evaporated. Recrystallization from methanol afforded 2.7 g. of colorless crystals, m.p. 91.5–92.5°.

Anal. Calcd. for $C_{16}H_{17}O_4N$: C, 66.88; H, 5.97. Found: C, 66.64; H, 5.95.

This enol gave a dark red color with ferric chloride. The infrared spectrum (chloroform) had a peak at 4.55 μ. No peaks representative of hydroxyl or carbonyl groups were apparent.

The infrared spectra of IIA and IIB were virtually identical in the region 8–10 μ.

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The Preparation of the Methylmethoxygermanes

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Johnson and Fritz have recently reported the preparation and properties of seven germanium tetraalkoxides[1]; before their work only two such compounds, tetraethoxygermane[2] and tetraphenoxygermane,[3] were known. This paper reports the synthesis of the three methylmethoxygermanes. These compounds, which are apparently the first alkylalkoxygermanes to be reported, complete the series $(CH_3)_4Ge$–$Ge(OCH_3)_4$.

The methylmethoxygermanes are colorless mobile liquids, with faint pleasant odors, soluble in all organic solvents tried. They are hydrolyzed rapidly by water or moist air to polymeric alkylgermanium oxides. The compounds are monomeric in the vapor state, and unlike the methylchlorogermanes,[4] their boiling points increase almost regularly with increasing molecular weight.

Experimental[5]

Methyltrimethoxygermane.—The preparation was carried out in a 500-ml. flask fitted with a reflux condenser and a dropping funnel, both protected from atmospheric moisture with drying tubes. To a solution of 13.3 g. (0.58 gram atom) of sodium in 125 ml. of methanol was added dropwise 34.6 g. (0.178 mole) of methyltrichlorogermane.[6] The mixture was heated to reflux for two hours. The methanol solution containing the product was then filtered from the precipitated NaCl under reduced pressure, using a sintered glass filter tube. The product was separated from methanol by fractional distillation through a 40-cm. helix-packed column. The yield was 21.9 g., or 66%.

Anal. Calcd. for $C_4H_{12}GeO_3$: C, 26.58; H, 6.69; mol. wt., 181. Found: C, 26.59; H, 6.72; mol. wt., 181.

TABLE I

COMPOUNDS OF THE SERIES $(CH_3)_4Ge$–$Ge(OCH_3)_4$

Formula	B.p. °C.	Mm.	$n^{25}D$	d^{25}_4
$(CH_3)_4Ge$[7]	43.2	736	1.3863	0.9661
$(CH_3)_3GeOCH_3$	87–88	753	1.401	1.075
$(CH_3)_2Ge(OCH_3)_2$	118–118.5	763	1.4093	1.207
$CH_3Ge(OCH_3)_3$	136.5–138	760	1.4053	1.264
$Ge(OCH_3)_4$[1]	148–150	722	1.3968	1.325

Dimethyldimethoxygermane.—This compound was prepared from dimethyldichlorogermane[6] and sodium methoxide in 77% yield, in the same way as in the preparation of methyltrimethoxygermane.

Anal. Calcd. for $C_4H_{12}GeO_2$: C, 29.16; H, 7.34; mol. wt., 165. Found: C, 28.98; H, 7.38; mol. wt., 171.

Trimethylmethoxygermane.—A Grignard reagent solution prepared from 51 g. (0.40 mole) of methyl iodide was added with stirring to a solution of 66 g. (0.40 mole) of dimethyldimethoxygermane in 300 ml. of ethyl ether, under an atmosphere of nitrogen. After standing overnight, the ethereal solution was filtered from the precipitated magnesium salts under nitrogen and fractionally distilled. However, none of the expected trimethylmethoxygermane was isolated. Instead, 9.5 g. of impure trimethyliodogermane came over at 136° as a heavy oil which liberated iodine on standing. Titration with base gave 47.0% I; C_3H_9GeI requires 51.9%.

Six grams (0.024 mole) of this product was then treated with sodium methoxide in methanol as in the previous preparations. Fractional distillation now gave 2.0 g. (56%) of trimethylmethoxygermane.

Anal. Calcd. for $C_4H_{12}GeO$: C, 32.30; H, 9.14; mol. wt., 149. Found: C, 32.31; H, 9.40; mol. wt., 152.

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