for 8 h at 5–10 °C. The mixture was worked up in the usual manner to give 16 mg (93%) of **2b** (*n* = 12, R^1 = Me) as an oil: bp 51.5–53.5 °C (0.005 mm, Kugelrohr); IR (neat) 3320 (OH), 1668 (C=C), 1460, 1380, 1015, 720 cm^{-1}; ^{1}H NMR (100 MHz) δ 1.32 (br s, 23, CH_2, OH), 1.68 (s, 3, CH_3), 2.04–2.15 (m, 2, CH_2), 4.28–4.54 (m, 1, CHO), 5.18 (d, 1, *J* = 10 Hz, HC=C). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.54; H, 12.55.

(*E*)- and (*Z*)-3-Methyl-2-cyclopentadecen-1-ones (11).[11] To a stirred suspension of pyridinium chlorochromate (30 mg, 0.11 mmol) in CH_2Cl_2 (1 mL) was added dropwise a solution of **2b** (*n* = 12, R^1 = Me; 15 mg, 0.063 mmol) in CH_2Cl_2 at 0–5 °C. The mixture was stirred for 30 min at 5 °C and for 2 h at room temperature and worked up in the usual manner to give 9.7 mg (65%) of **11** as an oil: bp 75.0–78.0 °C (0.005 mm, Kugelrohr) [lit.[11a] 100–105 °C (0.01 mm)]; IR (neat) 3050, 1685 (C=O), 1617 (C=C) cm^{-1}; ^{1}H NMR (100 MHz) δ 1.30 (br, 22, CH_2), 2.14 (s, 3, CH_3), 2.28, 2.41 (d, 2, *J* = 5 Hz, $COCH_2$), 6.17 (br s, 1, HC=C).

***dl*-Muscone.**[12] A mixture of **11** (7 mg, 0.03 mmol) and 10% palladium on charcoal in EtOH (1.5 mL) was treated with excess H_2 (2 mL). The mixture was filtered, and the filtrate was concentrated to give 6.8 mg (97%) of *dl*-muscone:[13] bp 77.5–79.0 °C (0.005 mm, Kugelrohr) [lit.[11a] 100–105 °C (0.01 mm)]; IR (neat) 1715 cm^{-1} (C=O); ^{1}H NMR (60 MHz) δ 0.92 (d, 3, *J* = 6 Hz, CH_3), 1.29 (br, 23, CH_2, CH), 2.00–2.52 (m, 4, CH_2).

Registry No.—(*E*)-**1a** (*n* = 12, R^1 = Me), 69832-58-2; (*Z*)-**1a** (*n* = 12, R^1 = Me), 69832-59-3; (*E*)-**1a** (*n* = 9, R^1 = Me), 69832-60-6; (*Z*)-**1a** (*n* = 9, R^1 = Me), 69832-61-7; **1a** (*n* = 4, R^1 = *n*-C_5H_{11}), 69832-62-8; **1a** (*n* = 2, R^1 = *n*-C_6H_{13}), 69832-63-9; **1b** (*n* = 3, R^1 = *n*-C_5H_{11}), 69832-64-0; (*E*)-**1c** (*n* = 12, R^1 = Me), 69832-65-1; (*Z*)-**1c** (*n* = 12, R^1 = Me), 69832-66-2; (*E*)-**1c** (*n* = 9, R^1 = Me), 69832-67-3; (*Z*)-**1c** (*n* = 9, R^1 = Me), 69832-68-4; **1c** (*n* = 4, R^1 = *n*-C_5H_{11}), 69832-69-5; **1c** (*n* = 3, R^1 = *n*-C_5H_{11}), 69855-40-9; **1c** (*n* = 2, R^1 = *n*-C_6H_{13}), 69832-70-8; (*E*)-**2a** (*n* = 12, R^1 = Me), 69832-71-9; (*Z*)-**2a** (*n* = 12, R^1 = Me), 69832-72-0; (*E*)-**2a** (*n* = 9, R^1 = Me), 69832-73-1; (*Z*)-**2a** (*n* = 9, R^1 = Me), 69832-74-2; **2a** (*n* = 4, R^1 = *n*-C_5H_{11}), 69832-75-3; **2a,** (*n* = 3, R^1 = *n*-C_5H_{11}), 69832-76-4; **2a** (*n* = 2, R^1 = *n*-C_6H_{13}), 69832-77-5; (*E*)-**2b** (*n* = 12, R^1 = Me), 69832-78-6; (*Z*)-**2b** (*n* = 12, R^1 = Me), 69832-79-7; (*E*)-**2c** (*n* = 12, R^1 = Me), 69832-80-0; (*Z*)-**2c,** (*n* = 12, R^1 = Me), 69832-81-1; (*E*)-**2c** (*n* = 9, R^1 = Me), 69832-82-2; (*Z*)-**2c,** (*n* = 9, R^1 = Me), 69832-83-3; **2c** (*n* = 3, R^1 = *n*-C_5H_{11}), 69832-84-4; **3a** (*n* = 12, R^2 = Me), 52794-21-5; **3a** (*n* = 9, R^2 = Me), 62939-87-1; **3a,** (*n* = 4, R^2 = Me), 52784-32-4; **3a** (*n* = 2, R^2 = Me), 10472, 24-9; **3b** (*n* = 12, R^1 = R^2 = Me), 69832-85-5; **3b** (*n* = 9, R^1 = R^2 = Me), 69832-86-6; **3b** (*n* = 4, R^1 = *n*-C_5H_{11}, R^2 = Me), 69832-87-7; **3b** (*n* = 2, R^1 = *n*-C_6H_{13}, R^2 = Me), 69832-88-8; **3b** (*n* = 3, R^1 = *n*-C_5H_{11}, R^2 = Et), 57026-68-3; **4a** (*n* = 12, R^1 = R^2 = Me), 69832-89-9; **4a** (*n* = 9, R^1 = R^2 = Me), 69832-90-2; **4a** (*n* = 4, R^1 = *n*-C_5H_{11}, R^2 = Me), 69832-91-3; **4a** (*n* = 3, R^1 = *n*-C_5H_{11}, R^2 = Et), 69832-92-4; **4a** (*n* = 2, R^1 = *n*-C_6H_{13}, R^2 = Me), 69832-93-5; **4b** (*n* = 12, R^1 = R^2 = Me), 69832-94-6; **4b** (*n* = 9, R^1 = R^2 = Me), 69832-95-7; **4b** (*n* = 4, R^1 = *n*-C_5H_{11}, R^2 = Me), 69832-96-8; **4b** (*n* = 3, R^1 = *n*-C_5H_{11}, R^2 = Et), 69832-97-9; **4b** (*n* = 2, R^1 = *n*-C_6H_{13}, R^2 = Me), 69832-98-0; (*E*)-**5** (*n* = 12, R^1 = Me), 69832-99-1; (*Z*)-**5** (*n* = 12, R^1 = Me), 69833-00-7; (*E*)-**5** (*n* = 9, R^1 = Me), 69833-01-8; (*Z*)-**5** (n = 9, R^1 = Me), 69833-02-9; **5** (*n* = 3, R^1 = *n*-C_5H_{11}), 69833-03-0; **6,** 69833-04-1; **7,** 69833-05-2; **8a,** 65898-58-0; **8b,** 69833-06-3; **9,** 69833-07-4; **10,** 69833-08-5; (*E*)-**11,** 58643-70-2; (*Z*)-**11,** 58643-71-3; *dl*-muscone, 956-82-1.

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Reaction of 2,3,4,6-Tetramethoxybenzaldehyde with Aluminum Chloride. Selective Cleavage at Position 2 and Selective Ether Exchange at Position 3

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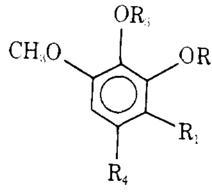
The cleavage of 2,3,4,6-tetramethoxybenzaldehyde, **1**, with aluminum chloride in ether to obtain the 2-hydroxy compound, **2**,[1] is accompanied by formation of appreciable amounts (38%) of a single ethoxy-containing compound. This compound is identified as **3**. A modification for a high yield preparation of pure **2** is described.

Polymethoxybenzaldehydes with 2-methoxy groups can cleave that group selectively with aluminum chloride.[2-4] Reichstein[2] formed the 2-hydroxy compound **4** from **5** using toluene as the solvent, but Robertson,[3] finding that toluene cleaved all the methoxy groups, used ether as the solvent.

To monocleave **1** to **2**, we tried Robertson's method. The cleavage product had a wide melting point range after some purification and showed ethoxy peaks in ^{1}H NMR. The simplicity of the spectra suggested a mixture containing a single ethoxy compound in 38% yield. Isolation of the dimethoxyethoxyhydroxybenzaldehyde, **3**, was accomplished via extraction with 5% sodium carbonate solution. Its identity was established by methylation and comparison with known ethoxytrimethoxybenzaldehydes. The ethoxy should be either in the 3 position (next to the phenol) or the 6 position (next to the formyl group). Accordingly, 3-ethoxy-2,4,6-trimethoxy- and 6-ethoxy-2,3,4-trimethoxybenzaldehydes, **6** and **7**, were prepared respectively from the phenols **8** and **9** via ethylation to **10** and **11** and formylation to **6** and **7**. By increasing the



	R_1	R_2	R_3	R_4
1	CHO	CH_3	CH_3	CH_3O
2	CHO	H	CH_3	CH_3O
3	CHO	H	CH_3CH_2	CH_3O
4	CHO	H	CH_3	H
5	CHO	CH_3	CH_3	H
6	CHO	CH_3	CH_3CH_2	CH_3O
7	CHO	CH_3	CH_3	CH_3CH_2O
8	H	CH_3	H	CH_3O
9	H	CH_3	CH_3	OH
10	H	CH_3	CH_3CH_2	CH_3O
11	H	CH_3	CH_3	CH_3CH_2O
12	CHO	H	H	CH_3O
13	CHO	$-CH_2-$		CH_3O

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molar ratio of $AlCl_3$/1 from 1.1 to 1.7–2.0, the amount of 3 could be increased to 55%.

To circumvent the ethoxy exchange, the cleavage was run in benzene at 50 °C where yields of pure 2 of up to 84% were realized. On refluxing in benzene, about 8% of dicleaved material, 12, was obtained, similar to that in acetophenones.[5] Identification of 12 was from conversion to its methylenedioxy derivative, 13.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Melting and boiling points are uncorrected. Nuclear magnetic resonance spectra were recorded at 90 MHz on a Varian EM-390 using Me_4Si as the internal standard. Infrared spectra were recorded on a Perkin-Elmer 457. Microanalyses were performed by M-H-W Laboratories, Garden City, Mich.

2-Hydroxy-3,4,6-trimethoxybenzaldehyde (2). To a solution of 51.0 g (0.226 mol) of 1[6] in 500 mL of dry benzene was added 33 g (0.248 mol) of anhydrous aluminum chloride. After being shaken for 5 min, the mixture was heated at 50 °C for 7.5 h. Water, 300 mL, was added, and the mixture was shaken to decompose the dark oil. Water, 2.5 L, benzene, 1 L, and 12 M hydrochloric acid, 125 mL, were added, and the mixture was stirred overnight. The clear colored phases were separated. The aqueous phase was extracted with ether and benzene. The combined organic phases were extracted six times with 100-mL portions of 5% sodium hydroxide solution. While being stirred and cooled, the basic solutions were acidified with 110 mL of 12 M hydrochloric acid. The tan solids were dissolved in 250 mL of hot methanol, diluted with 100 mL of hot water, and cooled to produce 40.0 g (84%) of **2** as yellow rods, mp 103–104 °C. Recrystallization from 25% methanol/water produced light yellow thick rods: mp 102.0–102.7 °C; IR (KBr) 2840, 1640, 1635 cm^{-1}; NMR ($CDCl_3$) δ 3.82, 3.89, 3.98 (s, 3 each, OCH_3), 5.97 (s, 1, ArH), 10.12 (s, 1, CHO), 12.27 (s, 1, OH).

Anal. Calcd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.70; H, 5.69.

4,6-Dimethoxy-3-ethoxy-2-hydroxybenzaldehyde (3). To a solution of 11.3 g (0.05 mol) of 1 in 600 mL of anhydrous ether was added a solution of 9.35 g (0.07 mol) of anhydrous aluminum chloride in 150 mL of anhydrous ether. The yellow suspension was shaken for 5 min forming a brown oil. After standing at room temperature overnight, the mixture was refluxed 8 h on the steambath. Water, 50 mL, was added and then 6 M hydrochloric acid, 25 mL. After being stirred overnight, the two clear colored phases were separated. The aqueous phase was extracted five times with ether. The combined ethereal solutions were extracted eight times with 25-mL portions of 5% sodium hydroxide solution. The basic washes were acidified with 6 M hydrochloric acid, 55 mL, producing 8.76 g (83%) of a mixture of **2** and **3** containing 38% **3** (from NMR). After being dissolved in 500 mL of ether, the mixture was extracted three times with 100-mL portions of 5% sodium carbonate solution. The ethereal phase was washed with saturated salt solution and dried with anhydrous sodium sulfate. Solvent removal yielded 3.96 g of tan-yellow solids: mp 86–106 °C; NMR ($CDCl_3$) showed 67% of **3** present. Recrystallization from 1:1 ethanol/water resulted in pure **3** as yellow rods: mp 116.3–117.1 °C; IR (KBr) 2850, 1635; NMR ($CDCl_3$) δ 1.36 (t, 3, CH_3, $J = 7.2$ Hz), 3.90, 3.97 (s, 3 each, OCH_3), 4.04 (q, 2, OCH_2), 5.99 (s, 1, ArH), 10.17 (s, 1, CHO), 12.30 (s, 1, OH).

Anal. Calcd for $C_{11}H_{14}O_5$: C, 58.40; H, 6.24. Found: C, 58.36; H, 6.28. Acidification of the sodium carbonate washes and recrystallization of the solid produced **2** identical with that produced in aluminum chloride/benzene cleavage.

2-Ethoxy-1,3,5-trimethoxybenzene (10). 2,4,6-Trimethoxyphenol[4] reacts with ethyl sulfate and sodium hydroxide solution forming colorless rods from cyclohexane: mp 48.8–49.4 °C; IR (KBr) 2840, 1235, 1225, 1210 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (t, 3, CH_3, $J = 7.2$ Hz), 3.80 (s, 3, OCH_3), 3.85 (s, 6, OCH_3), 4.00 (q, 2, OCH_2), 6.19 (s, 2, ArH).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.52; H, 7.47.

5-Ethoxy-1,2,3-trimethoxybenzene (11). Antiarol[7] reacts with ethyl iodide, potassium carbonate, and acetone forming a colorless oil: bp 111 °C (1.7 torr); IR (film) 2850, 1230 cm^{-1}; NMR ($CDCl_3$) δ 1.37 (t, 3, CH_3, $J = 7.0$ Hz), 3.80 (s, 3, OCH_3), 3.83 (s, 6, OCH_3), 3.97 (q, 2, OCH_2), 6.18 (s, 2, ArH).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.46; H, 7.62.

3-Ethoxy-2,4,6-trimethoxybenzaldehyde (6). A Vilsmeier reaction[8] on **10** produced colorless rods from cyclohexane: mp 60.0–60.9 °C; IR (KBr) 1670, 1255, 1215 cm^{-1}; NMR ($CDCl_3$) δ 1.33 (t, 3, CH_3, $J = 7$ Hz), 3.89, 3.93, 3.94 (s, 3 each, OCH_3), 3.99 (q, 2, OCH_2), 6.27 (s, 1, ArH), 10.30 (s, 1, CHO).

Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 60.11; H, 6.75. Also formed from **3** on reaction with methyl sulfate, potassium carbonate and acetone.

6-Ethoxy-2,3,4-trimethoxybenzaldehyde (7). A Vilsmeier reaction on **11** produced from benzene and then 25% methanol/water colorless microscopic rods: mp 57.7–58.5 °C; IR (KBr) 2850, 1680, 1250, 1200 cm^{-1}; NMR ($CDCl_3$) δ 1.47 (t, 3, CH_3, $J = 7$ Hz), 3.83 (s, 3, OCH_3), 3.96 (s, 6, OCH_3), 4.12 (q, 2, OCH_2), 6.30 (s, 1, ArH), 10.40 (s, 1, CHO).

Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.97; H, 6.75.

2,3-Dihydroxy-4,6-dimethoxybenzaldehyde (12). The procedure for the preparation of **2** was followed but the reaction mixture was refluxed for 8 h. Evaporation of the mother liquors from recrystallization left well-formed golden crystals, mp 114–137 °C. Further crystallization from benzene produced rhombahedral yellow plates: mp 147.8–148.3 °C; IR (KBr) 3340, 2850, 1660 cm^{-1}; NMR ($CDCl_3$) δ 3.90, 4.03 (s, 3 each, OCH_3), 5.13 (s, 1, 3-OH), 6.03 (s, 1, ArH), 10.20 (s, 1, CHO), 12.25 (s, 1, 2-OH).

Anal. Calcd for $C_9H_{10}O_5$: C, 54.55; H, 5.09. Found: C, 54.77; H, 4.99.

4,6-Dimethoxy-2,3-methylenedioxybenzaldehyde (13). From **12** using the procedure of Bonthrone and Cornforth[9] colorless needles formed: mp 166–167 °C; IR (KBr) 2880, 2775, 1675 cm^{-1}; NMR ($CDCl_3/C_6D_6$) δ 3.35, 3.57 (s, 3 each, OCH_3), 5.56 (s, 2, CH_2O_2), 5.70 (s, 1, ArH), 10.32 (s, 1, CHO).

Anal. Calcd for $C_{10}H_{10}O_5$: C, 57.14; H, 4.80. Found: C, 57.27; H, 4.78.

Registry No.—**1**, 41038-46-4; **2**, 65162-31-4; **3**, 69832-50-4; **6**, 69832-51-5; **7**, 69832-52-6; **8**, 20491-92-3; **9**, 642-71-7; **10**, 69832-53-7; **11**, 69832-54-8; **12**, 69832-55-9; **13**, 69832-56-0.

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(1) The monocleaved product is a hydroxytrimethoxybenzaldehyde. The peak in the NMR at 12.27 shows the hydroxy group is hydrogen bonded to the adjacent aldehyde. Only two compounds are possible, the 2-hydroxy-3,4,6-trimethoxybenzaldehyde and the 6-hydroxy-2,3,4-trimethoxybenzaldehyde. This latter compound is known,[7] having mp 65 °C. This leaves the 2-hydroxy compound as the only other possibility.

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Vitamin B_{12s} Catalyzed Dechlorination of 1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethane. Novel Synthesis of Substituted Stilbenes

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The bioinorganic chemistry of vitamin B_{12} and related molecules, in aqueous and micellar environments, is well documented.[1–6] From a purely chemical point of view, vitamin B_{12s} is an extraordinary nucleophile whose participation in dechlorination reactions would not be unexpected. It is our purpose to report a novel, vitamin B_{12s}-catalyzed synthesis of substituted stilbenes starting with readily available materials.

The reaction consists essentially of the addition of a methanol solution of 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane, DDD, to an aqueous solution of vitamin B_{12s} under

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