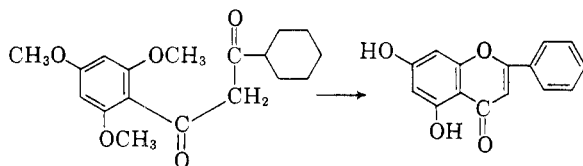


dihydroxyflavone) by means of aqueous HI also effects complete demethylation:<sup>3,4</sup>



On the other hand, our cyclization technique with potassium iodide in orthophosphoric acid constitutes an application of new materials to an old synthetic route, with the indicated bonus of maintaining the excess alkoxy groups intact. The structure of VIII was confirmed by elementary analyses, oximation to a mono-oxime, and the infrared spectrum for the carbonyl group.

#### EXPERIMENTAL

**2,4-Dimethoxyacetophenone (II).** This starting material was prepared by an adaptation of Gardner's technique<sup>5</sup> for the *C*-acetylation of aromatic compounds. A mixture of 41.4 g. (0.3 mole) of *m*-dimethoxybenzene (Eastman), 21.6 g. (0.36 mole) of glacial acetic acid, and 400 g. of polyphosphoric acid became homogeneous after the initiation of agitation, turning yellow, then red. The reaction mass was kept at 50–53° for 3 hr., then drowned in 1200 ml. of ice water. From the ether extract, after drying over anhydrous sodium sulfate, there was obtained 46.5 g. (86.1%) of 2,4-dimethoxyacetophenone: b.p., 134–137°/3 mm. m.p. 40–43°. A melting point given in the literature<sup>6</sup> is 44°.

**2,4-Dimethoxybenzoic acid.** This intermediate to the ethyl ester (III) was prepared by a modification of the procedure of Robinson and Venkataraman,<sup>7</sup> entailing treatment of  $\beta$ -resorcylic acid with 6 portions of dimethyl sulfate and concentrated aqueous alkali. Thus, from 154 g. (1.0 mole) of  $\beta$ -resorcylic acid (Koppers), 1675 g. (13.3 moles) of dimethyl sulfate, and 612 g. (15.3 moles) of sodium hydroxide in 1.3 l. of water, there was obtained 146 g. (80%) of 2,4-dimethoxybenzoic acid, melting at 99–104° (lit. value, 108°).<sup>7</sup>

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>O<sub>4</sub>: neut. equiv., 182.0. Found: neut. equiv., 180.0.

**Ethyl 2,4-dimethoxybenzoate (III).** A mixture of 126 g. (0.69 mole) of 2,4-dimethoxybenzoic acid, 127 g. (2.76 moles) of ethanol, 277 ml. of benzene, and 3 ml. of 100% sulfuric acid was reacted according to a modified procedure of Perkins and Schiess<sup>8</sup> to yield 89 g. (66%) of ethyl 2,4-dimethoxybenzoate, distilling at 143–147°/3.5 mm.

*Anal.* Calcd. for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub>: sapon. equiv., 210.0. Found: sapon. equiv., 205.0.

**2,2',4,4'-Tetramethoxydibenzoylmethane (IV).** A 0.5-mole batch of sodamide was freshly prepared in a reactor, consisting of a 250 ml., 3-necked, ground-glass flask, immersed in a Dry Ice bath and equipped with a Dry Ice condenser, dropping funnel, and thermometer. The excess ammonia was removed by distillation and replaced simultaneously with anhydrous ethyl ether. To the ethereal suspension of sodamide was added 45 g. (0.25 mole) of 2,4-dimethoxyacetophenone in 42 ml. of ether during a 10-min. period. Five min. later, a solution of 52.5 g. (0.25 mole) of ethyl 2,4-di-

methoxybenzoate was added in the same manner. After refluxing overnight, the mass was drowned in ice water containing hydrochloric acid; the excess ether distilled off; and a red-yellow solid filtered off. Recrystallization of the latter gave 32 g. (37.2%) of a yellow, crystalline material melting at 131–134°;  $\lambda_{\text{max}}^{\text{CCl}_4}$  1655 cm.<sup>-1</sup> (6.04 $\mu$ ) and 1605 cm.<sup>-1</sup> (6.24 $\mu$ ).

*Anal.* Calcd. for C<sub>19</sub>H<sub>20</sub>O<sub>6</sub>: C, 66.2; H, 5.81. Found: C, 65.10, 65.32; H, 5.64, 5.79.

**7,2',4'-Trimethoxyflavone (VIII).** A small flask, fitted with an agitator, a reflux condenser, and a dropping funnel was charged with 1.2 g. of phosphorus pentoxide and 5.1 g. (0.045 mole) of 85% phosphoric acid. After the 100% phosphoric acid was cooled to room temperature, 5.0 g. (0.03 mole) of finely ground potassium iodide and 1.7 g. (0.005 mole) of 2,2',4,4'-tetramethoxydibenzoylmethane were added in sequence. The reaction mixture was agitated at 105–110° for 0.5 hr., drowned in ice water, and the precipitate filtered off. The latter, after recrystallization from aqueous ethanol, gave 1.4 g. (75%) of the white, crystalline flavone, melting at 143.5–145.5°;  $\lambda_{\text{max}}^{\text{CCl}_4}$  1635 cm.<sup>-1</sup> (6.11 $\mu$ );  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  236 m $\mu$  ( $\epsilon$ , 2200);  $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$  334 m $\mu$  ( $\epsilon$ , 2450).

*Anal.* Calcd. for C<sub>18</sub>H<sub>16</sub>O<sub>5</sub>: C, 69.23; H, 5.13. Found: C, 69.01, 69.18; H, 5.24, 5.19.

**7,2',4'-Trimethoxyflavone oxime.** The oxime was prepared by heating a mixture of 2 g. of the flavone and 3 g. of hydroxylamine hydrochloride and 3 ml. of pyridine on a steam bath for 4 hr. The reaction mixture was cooled and drowned in dilute acetic acid. The filtered product, after two recrystallizations from ethanol, yielded 1.7 g. (86%) of a white, crystalline material, melting at 204–207°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>17</sub>NO<sub>5</sub>: N, 4.28. Found: N, 4.14.

**Attempted preparation of 2,2'-dihydroxy-4,4'-dimethoxydibenzoylmethane.** The selective demethylation of the methoxy group ortho to the carbonyl in 2,4-dimethoxybenzophenone is known<sup>9</sup> and served as the basis for the attempted demethylations of IV to V. Reactions with aluminum chloride and 48% hydrobromic acid failed, yielding intractable gums or tars from which no crystalline material could be obtained.

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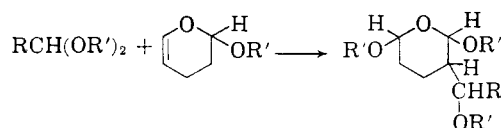
(9) H. Kauffmann and P. Panwitz, *Ber.*, **43**, 1205 (1910).

### Preparation of 2,6-Dialkoxy-3-(1-alkoxyalkyl)tetrahydropyrans

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The acid-catalyzed addition of acetals to dihydropyran to give 2-alkoxy-3-(1-alkoxyalkyl)tetrahydropyrans is well known.<sup>1</sup> The purpose of this note is to report the extension of this reaction to include the addition of acetals to 2-alkoxy-3,4-dihydro-2H-



(1) R. Paul and S. Tchelitcheff, *Bull. soc. chim. France*, 1155 (1950).

(4) T. Emilewicz, St. v. Kostanecki, and J. Tambor, *Ber.*, **32**, 2449 (1899).

(5) P. D. Gardner, *J. Am. Chem. Soc.*, **77**, 4674 (1955).

(6) F. Mauthner, *J. prakt. Chem.*, 119, 311 (1928).

(7) R. Robinson and K. Venkataraman, *J. Chem. Soc.*, 61 (1929).

(8) W. H. Perkins and E. Schiess, *J. Chem. Soc.*, 159 (1904).

pyrans. Good yields of 2,6-dialkoxy-3-(1-alkoxy-alkyl)tetrahydropyrans are obtained.

The latter compounds are readily converted by known methods to 2-alkylideneglutaraldehydes and 2-alkyl-1,5-pentanediois. Since many 2-alkoxy-3,4-dihydro-2*H*-pyrans are obtainable,<sup>2</sup> the reactions described here make available a wide variety of 2-alkylideneglutaraldehydes and their derivatives.

#### EXPERIMENTAL

*2,6-Diethoxy-3-(1-ethoxy-2-methylpropyl)tetrahydropyran.* Isobutyraldehyde diethyl acetal, 219 g. (1.5 moles), was combined with 3 ml. of boron trifluoride etherate and cooled to 5°. Over a 45-min. period, 2-ethoxy-3,4-dihydro-2*H*-pyran, 128 g. (1 mole), was added with stirring and cooling to maintain the temperature at 5–10°. Stirring was continued for 30 min. without cooling while the temperature rose to 18°. The catalyst was neutralized by adding a solution of 20 g. of potassium carbonate in 30 ml. of water, and the organic phase was separated and distilled. After recovery of 73 g. of isobutyraldehyde diethyl acetal, 174 g. (63.5%) of 2,6-diethoxy-3-(1-ethoxy-2-methylpropyl)tetrahydropyran, b.p. 86–89° (ca. 1 mm.),  $n_D^{20}$  1.4400, was obtained.

*Anal.* Calcd. for  $C_{15}H_{20}O_4$ : C, 65.66; H, 11.02. Found: C, 65.54; H, 10.98.

Treatment of the product with 2,4-dinitrophenylhydrazine reagent gave the bis(2,4-dinitrophenylhydrazone) of 2-isobutylideneglutaraldehyde, m.p. 217–219°.

*Anal.* Calcd. for  $C_{21}H_{22}N_8O_8$ : C, 49.03; H, 4.31. Found: C, 49.06; H, 4.52.

*2,6-Diethoxy-3-(1-ethoxypropyl)tetrahydropyran.* Addition of 2-ethoxy-3,4-dihydro-2*H*-pyran, 250 g. (2 moles), to propionaldehyde diethyl acetal, 290 g. (2.2 moles), containing 2 ml. of boron trifluoride etherate, as described above, gave 405 g. (78%) of 2,6-diethoxy-3-(1-ethoxypropyl)tetrahydropyran, b.p. 79–82° (ca. 1 mm.),  $n_D^{20}$  1.4378.

*Anal.* Calcd. for  $C_{14}H_{20}O_4$ : C, 64.58; H, 10.84. Found: C, 64.39; H, 10.96.

*2,6-Diethoxy-3-(1-ethoxybutyl)tetrahydropyran.* This compound (b.p. 93–95° at ca. 1 mm.,  $n_D^{20}$  1.4389) was obtained in 64% yield from butyraldehyde diethyl acetal as described above.

*Anal.* Calcd. for  $C_{15}H_{20}O_4$ : C, 65.66; H, 11.02. Found: C, 65.48; H, 11.12.

*2-Butyl-1,5-pentanediol.* A mixture of 500 ml. of *p*-dioxane, 88.5 ml. of water, 17.5 ml. of concentrated hydrochloric acid, and 250 g. (0.92 mole) of 2,6-diethoxy-3-(1-ethoxybutyl)tetrahydropyran was stirred at 45° until it became homogeneous, and then stirred for an additional 4 hr.<sup>3</sup> The mixture was then neutralized by the addition of solid sodium bicarbonate and filtered. The filtrate was subjected to hydrogenation over Raney nickel at 150° and 100 atm. The catalyst was removed by filtration, and the filtrate was distilled to obtain 107.5 g. (73%) of 2-butyl-1,5-pentanediol, b.p. 105–109° (ca. 1 mm.),  $n_D^{20}$  1.4603.

*Anal.* Calcd. for  $C_9H_{20}O_2$ : C, 67.45; H, 12.57. Found: C, 67.28; H, 12.32.

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(2) See, for example, R. I. Longley, Jr., and W. S. Emerson, *J. Am. Chem. Soc.*, **72**, 3079 (1950).

(3) R. I. Longley, Jr., W. S. Emerson, and T. C. Shafer, *J. Am. Chem. Soc.*, **74**, 2012 (1952).

## Chlorination of 1,3-Diacetylurea and of Barbituric Acid

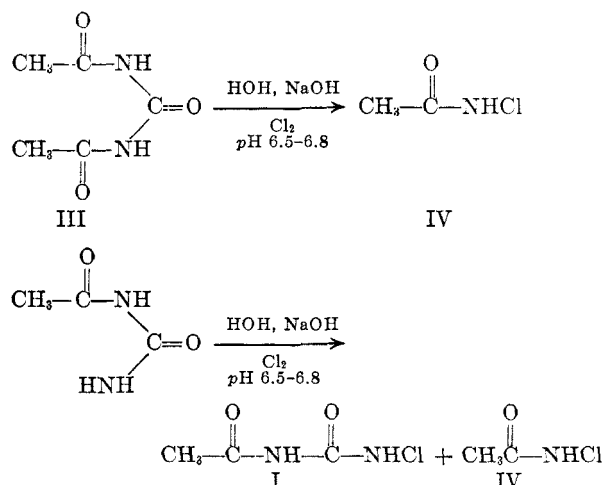
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1-Acetyl-3-chlorourea (I) is readily made by the chlorination of acetylurea in aqueous solution.<sup>1</sup> The compound decomposes with considerable vigor at 155–156°. It was thought that 1,3-diacetyl-1,3-dichlorourea (II) might be reasonably stable by virtue of the fact that the chlorine would be bound to imidic nitrogen atoms.

Attempts were made to prepare II by the chlorination of 1,3-diacetylurea (III) in an aqueous phase over a variety of *pH* ranges. Saturation of an aqueous solution of III with chlorine but without *pH* control gave recovered III as the only identifiable product. When III was chlorinated in such a fashion that the *pH* was maintained in the range 7–9 during the reaction, no product containing available chlorine was detected. The available chlorine containing product resulting from chlorination at *pH* 6–7 was shown to be *N*-chloroacetamide (IV).<sup>2–6</sup> Maintaining the *pH* at about 5 resulted in the formation of a yellow oil which was immediately deliberately destroyed by the addition of excess sodium hydroxide solution. The yellow oil may have been the explosive nitrogen trichloride or the oily, yellow *N,N*-dichloroacetamide.<sup>4</sup>

Saturation with chlorine, of an aqueous solution of acetylurea without *pH* control resulted in the formation of minute droplets of yellow oil which exploded upon being subjected to mechanical



(1) F. D. Chattaway and D. F. S. Wunsch, *J. Chem. Soc.*, **95**, 129 (1909).

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(3) C. Mauguin, *Annales de Chimie*, [8] **22**, 305 (1911).

(4) E. Boismenu, *Annales de Chimie*, [9] **9**, 161 (1918).

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(6) G. H. Coleman, R. L. Peterson, and G. F. Goheen, *J. Am. Chem. Soc.*, **58**, 1874 (1936).