

the form

$$b_0 + \frac{\epsilon_1}{b_1} + \dots + \frac{\epsilon_v}{b_v} + \dots + \frac{\epsilon_{v+r}}{b_{v+r}} + \dots$$

$$+ \frac{\epsilon_{2v}}{2b_0}, \text{ where}$$

$$b_v = 2, \epsilon_v = -1, b_{v-1} = b_{v+1} + 1,$$

$$\epsilon_{v+1} = 1 \text{ and}$$

$b_{v+r} = b_{v-r}, \epsilon_{v+r} = \epsilon_{v-r+1} (v \geq r > 1)$   
which give the symmetries for  $b$ 's and  $\epsilon$ 's.

(vi) The period of the square-root of a non-square positive integer has an even number of terms in the case contemplated in (v); and the denominators of the complete quotients up to the end of the period form a symmetric sequence of an odd number of terms with the middle term greater than 4.

*Example:*  $\sqrt{58} = 8 - \frac{1}{3} - \frac{1}{2} + \frac{1}{2} - \frac{1}{6}$  and  
the denominators of 2nd, 3rd and 4th complete quotients can be verified to be 6, 7, 6 respectively.

4. Associated with this new continued fraction there is a theory of reduced quadratic forms, which remains to be fully worked out. The complete system of indefinite, primitive reduced forms for any given non-square positive integral determinant  $R$  consists of forms of the type (A, B, C) satisfying one of the following three sets of conditions:

- (i)  $B > 0, A^2 + \frac{1}{4}C^2 < R, C^2 + \frac{1}{4}A^2 < R$   
(ii)  $B = |C| + \frac{1}{2}|A| > \sqrt{R}, |A| < |C|,$   
 $C^2 + \frac{1}{4}A^2 = R$   
(iii)  $B = |A| - \frac{1}{2}|C| < \sqrt{R}, |A| > |C|,$   
 $A^2 + \frac{1}{4}C^2 = R$

If  $A^2 + \frac{1}{4}C^2 = R = C^2 + \frac{1}{4}A^2$ , the form (A, B, C) is not primitive except when  $R = 5$ .

A. A. KRISHNASWAMI AYYANGAR.  
Maharaja's College,  
Mysore,  
May 27, 1938.

### Friedel-Crafts Reaction with Diethers of Resorcinol.

SIMONIS AND LEAR<sup>1</sup> claimed that O-diethylresorcinol with cinnamoyl chloride in presence of aluminium chloride gives 2:6-diethoxyphenyl styryl ketone, the cinnamoyl radical entering the nucleus in the 2-position between the two alkoxy groups. Simonis and Danisewski<sup>2</sup> made a similar claim for

O-dimethylresorcinol, and cinnamoyl and phenylpropionyl chlorides.

On general grounds direct substitution in the 2-position of resorcinol is unlikely; acetyl chloride for example enters the 4-position. A re-examination of the work has shown that cinnamoyl chloride also enters in the 4-position to give chalkones identical with those obtained from the corresponding O-dialkylresacetophenones by condensation with benzaldehyde; further the chalkones obtained from 2-acetyl-O-dialkylresorcinols and benzaldehyde differ from those described by Simonis. The whole of the work is under process of repetition. In the preparation of O-diethyl-2-acetylresorcinol indications of nuclear ethylation have been obtained.

It may be mentioned that Monti<sup>3</sup> claims that  $\beta$ -naphthyl methyl ether is substituted by cinnamoyl chloride in the 3-position; this again is doubtful; entry in the 1-position is more likely.

D. C. MOTWANI.  
V. V. BODANI.  
T. S. WHEELER.

Royal Institute of Science,  
Bombay,  
May 12, 1938.

<sup>1</sup> *Ber.*, 1926, 59, 2912.

<sup>2</sup> *Ibid.*, 1926, 59, 2916.

<sup>3</sup> *Gazz. chim. ital.*, 1930, 60, 43.

### Preferential Demethylation of Methoxyl Ortho to a Keto-group.

PREFERENTIAL demethylation of a methoxyl group situated in the ortho-position to a keto-group is known to be effected by treatment with aluminium chloride. It has now been found that such preferential demethylation can be achieved in satisfactory yield if the ketone is kept for some twenty-four hours in cold solution with hydrogen iodide in acetic anhydride or with hydrogen bromide in glacial acetic acid. For example, when a mixture of 2:4:6-trimethoxyacetophenone (5 g.), hydriodic acid (d., 1.7; 40 c.c.) and acetic anhydride (40 c.c.) which had been kept in the cold for 24 hours is diluted with sodium hydrogen sulphite solution, 2-hydroxy-4:6-dimethoxyacetophenone is obtained in 80 per cent. yield. The usual method employing aluminium chloride has here been found to give 60 per cent. yield.

Alkoxyated derivatives of *o*-methoxyphenyl styryl ketones can also be preferentially demethylated to the  $\sigma$ -hydroxy-compounds in this manner.

W. A. HUTCHINS.  
T. S. WHEELER.

Royal Institute of Science,  
Bombay,  
May 12, 1938.

Flavones from the Dibromides of  
*o*-Hydroxyphenyl Styryl Ketones. A  
Modified Synthesis of Apigenin and  
Luteolin.

It has previously been pointed out<sup>1</sup> that the dibromides of certain *o*-hydroxyphenyl styryl ketones which normally yield benzylidencoumaranones only on treatment with alcoholic alkali, can be converted into flavones by simple heating. It has now been found by several workers in this laboratory that better yields of the flavones can be obtained if the hydroxy-dibromide is treated with alcoholic potassium cyanide. Further, *o*-hydroxyphenyl  $\alpha$ -bromo- $\beta$ -ethoxy- $\beta$ -alkoxyphenylethyl ketones which give benzylidencoumaranones with alkali hydroxide or carbonate in presence of hot or cold acetone or alcohol, give flavones with alcoholic potassium cyanide.

2-Hydroxy-4 : 6-dimethoxyphenyl *p*-methoxystyryl ketone on bromination gives 5-bromo-2-hydroxy-4 : 6-dimethoxyphenyl  $\alpha\beta$ -dibromo- $\beta$ -*p*-anisylethyl ketone which on heating yields 6-bromo-5 : 7 : 4'-trimethoxyflavone; this with hydriodic acid gives apigenin (5 : 7 : 4'-trihydroxyflavone). Luteolin (5 : 7 : 3' : 4'-tetrahydroxyflavone) has been synthesised by heating 5-bromo-2-hydroxy-4 : 6-dimethoxyphenyl  $\alpha\beta$ -dibromo- $\beta$ -3 : 4-dimethoxyphenyl ethyl ketone with alcoholic potassium cyanide and treating the resulting bromoflavone with hydriodic acid.

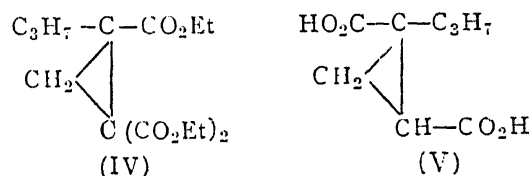
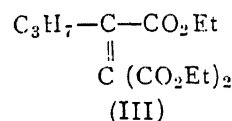
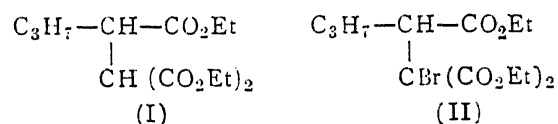
The synthesis of 5 : 7 : 2' : 4'-tetrahydroxy-flavone which is thought to be lotoflavin is now in hand.

W. A. HUTCHINS.  
T. S. WHEELER.

Royal Institute of Science,  
Bombay,  
May 12, 1938.

A New Method of Synthesis of  
Umbellularic Acid.

UMBELLULARIC acid, a degradation product of the naturally occurring bicyclic ketone umbellulone, has been synthesised by two methods.<sup>1,2</sup> It has now been synthesised by a convenient method starting from ethyl  $\alpha$ -isopropyl- $\alpha'$ -carbethoxy succinate (I) which gives readily the bromo-compound (II) (b.p. 155-56°/3 mm.; Found: Br, 21.40; Calc.: Br, 21.86 per cent.). The bromo-compound (II) loses a molecule of hydrobromic acid by the action of diethylaniline yielding ethyl isopropyl-carboxyfumarate (III), b.p. 135-40°/3 mm., which readily adds on a molecule of diazomethane to yield the cyclopropane-tricarboxylic ester (IV) (b.p. 148-50°/3 mm.; Found: C, 59.46; H, 8.34; Calc.: C, 60.0; H, 8.0 per cent.). The triester (IV) on being boiled with hydrochloric acid (18 per cent.) during eight hours got hydrolysed and decarboxylated and yielded *trans*-umbellularic acid (V) (m.p. 190-92°; Found: C, 55.63; H, 7.26; Calc.: C, 55.81; H, 7.0 per cent.). The *trans*-acid (V) has been converted into the *cis*-variety (monohydrate, m.p. 94-95°) by treating with acetyl chloride and its identity has been proved by taking mixed m.p. with a genuine sample obtained by older methods.



P. C. GUHA.  
M. S. MUTHANNA.

Department of Organic Chemistry,  
Indian Institute of Science,  
Bangalore,  
May 3, 1938.

<sup>1</sup> *Curr. Sci.*, 1937, 5, 475; *J.C.S.*, 1937, 1800.

<sup>1</sup> Rydon, *J.C.S.*, 1936, 829.

<sup>2</sup> Ranganathan, *J. Ind. Chem. Soc.*, 1936, 13, 419.  
Simonsen, *J.C.S.*, 1936, 828.