CCXLIII.—*The Intermolecular Condensation of Styryl Methyl Ketones. Part I.*

By ROBERT DICKINSON, ISIDOR MORRIS HEILBRON, and FRANCIS IRVING.

IN a previous investigation (Dickinson and Heilbron, this vol., p. 14), 3 : 4-dimethoxystyryl methyl ketone was required. Apparently three different substances, m. p.'s 168° (Francesconi and Cusmano, *Gazzetta*, 1908, **38**, ii, 70), 85—86°, and 91—92° (Ryan and Plunkett, *Proc. Roy. Irish Acad.*, 1916, **32**, *B*, 199; Kaufmann and Radosević, *Ber.*, 1916, **49**, 675), are recorded in the literature under this name, all having been prepared by the alkali condensation of veratraldehyde with acetone.

We have now investigated these compounds in detail. The second and the third are undoubtedly identical, the true melting point being 86°. This compound is definitely 3 : 4-dimethoxystyryl methyl ketone, for (1) its molecular weight, determined ebullioscopically, is normal; (2) in the presence of hydrogen chloride, it condenses with 2-naphthol-1-aldehyde, giving 3-3′ : 4′-dimethoxystyryl-β-naphthapyrylium chloride (Dickinson and Heilbron, *loc. cit.*); (3) it may be prepared by the methylation of 3-methoxy-4-hydroxystyryl methyl ketone; (4) it absorbs one molecule of bromine (the dibromide, however, could not be isolated); and (5) it readily condenses with veratraldehyde, in the presence of alkali, giving 3 : 3′ : 4 : 4′-tetramethoxydistyryl ketone, identical with the product obtained by Stobbe and Haertel (*Annalen*, 1909, **370**, 104), the constitution of which we have now confirmed by the preparation of its tetrabromide. Guimbal (*Dipl. et Sup.*, No. 212, Paris, 1921; compare Faillebin, *Ann. Chim.*, 1925, 4, 445) has come to the same conclusion, but only on the results of analysis and cryoscopy; he records 84° as the melting point. Lapworth and Wykes (J., 1917, **111**, 790) also must certainly have had this same ketone in their hands, as was shown by the ease with which it was oxidised to dimethylcaffeic acid. They do not, however, give the method of preparation, or record the melting point of their product, but only refer to Francesconi and Cusmano (*loc. cit.*), whose product is entirely different and cannot yield dimethylcaffeic acid.

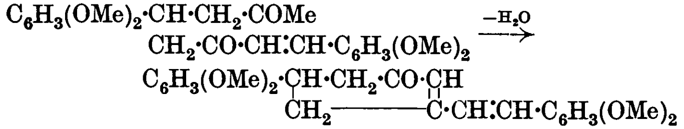
The compound described by Francesconi and Cusmano (*loc. cit.*) has also been obtained by other workers, who, beyond stating that it is not veratrylideneacetone and making suggestions as to its possible constitution, have not investigated it experimentally. It is regarded by Ryan and Plunkett (*loc. cit.*) as an isomeric form of the styryl ketone, by Kaufmann and Radosević (*loc. cit.*) as the corresponding distyryl ketone, and by Guimbal (*loc. cit.*) as a compound of 3 : 4-dimethoxystyryl methyl ketone and acetone. Francesconi and Cusmano (*loc. cit.*) do not record any analytical values for their compound, or for its alleged condensation product with cinnamaldehyde.

We have now found that in addition to its direct preparation from veratraldehyde and acetone, the 168°-compound may be obtained by treating 3 : 4-dimethoxystyryl methyl ketone with alkali, acetone being used as solvent in order to minimise the production of the distyryl ketone through scission (compare Heilbron and Buck, J., 1921, **119**, 1503). Our analyses show that the substance is formed according to the equations:

$$\text{(A)}\ 2C_6H_3(OMe)_2{\cdot}CHO + 2Me_2CO = C_{24}H_{26}O_5 + 3H_2O$$
$$\text{(B)}\ 2C_6H_3(OMe)_2{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_3 = C_{24}H_{26}O_5 + H_2O.$$

From a knowledge of the addition reactions of unsaturated ketones, the first stage in equation (B) is undoubtedly represented by formation of the compound (I) through simple addition at the αβ-ethenoid linkage.

(I).



$$\begin{array}{l} C_6H_3(OMe)_2\cdot CH\cdot CH_2\cdot COMe \\ \quad CH_2\cdot CO\cdot CH{:}CH\cdot C_6H_3(OMe)_2 \end{array} \xrightarrow{-H_2O} \begin{array}{l} C_6H_3(OMe)_2\cdot CH\cdot CH_2\cdot CO\cdot CH \\ \qquad CH_2 \text{———} C\cdot CH{:}CH\cdot C_6H_3(OMe)_2 \end{array}$$

(II.)

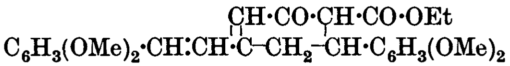
Many examples of such addition reactions are known; *e.g.*, Cornelson and Kostanecki (*Ber.*, 1896, **29**, 240) treated a mixture of 2-hydroxystyryl phenyl ketone and acetophenone with alkali and obtained 2-hydroxybenzylidenediacetophenone:

$$OH\cdot C_6H_4\cdot CH{:}CH\cdot COPh \xrightarrow{CH_3\cdot COPh} OH\cdot C_6H_4\cdot CH(CH_2\cdot COPh)_2.$$

Styryl and distyryl ketones add on acetoacetic ester and other keto-esters in precisely the same way, although secondary reactions occur afterwards (compare Heilbron and co-workers, J., 1924, **125**, 340, 2064; 1925, **127**, 2159; this vol., p. 918). The second stage of reaction (B) consists in the elimination of a molecule of water from compound (I), and this would almost certainly occur in such a manner as to yield the *cyclo*hexenone derivative (II).

The reactions of the 168°-compound are in full agreement with this formulation. We have determined its molecular weight, which is normal, and prepared its semicarbazone. It readily absorbs two molecules of bromine with exhibition of halochromy, but we have been unable to isolate the tetrabromide in a state of purity. Finally, full confirmation of formula (II) has been reached by the synthesis of the compound in the following way. 3 : 3′ : 4 : 4′-Tetramethoxydistyryl ketone was condensed with acetoacetic ester by means of sodium ethoxide (compare Heilbron and co-workers, *loc. cit.*); *ethyl* 3-mp-*dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ^5-cyclo*hexen-1-one-2-carboxylate* (III) was then readily obtained in good yield. On treatment of this with 20% sulphuric acid, the carbethoxyl was eliminated with production of the free *cyclo*hexenone (II), which was identical in all respects with the compound described by Francesconi and Cusmano.

(III.)

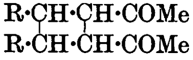


$$\begin{array}{l} \qquad\qquad\qquad\qquad\quad CH\cdot CO\cdot CH\cdot CO\cdot OEt \\ C_6H_3(OMe)_2\cdot CH{:}CH\cdot C\text{—}CH_2\text{—}CH\cdot C_6H_3(OMe)_2 \end{array}$$

We have attempted to obtain by similar means compounds analogous to (II), and for this purpose we prepared the *ethyl*, n-*propyl*, iso*propyl*, and *benzyl* ethers of 3-methoxy-4-hydroxystyryl methyl ketone. On treating these with alkali, we obtained the homologue of (II) in only one case—the *n*-propyl compound—and its reactions are in harmony with such a structure. An abnormal result was obtained with 3-*methoxy*-4-*benzyloxystyryl methyl ketone*, treatment with alkali yielding a new substance (m. p. 174—175°) which gave analytical results for 3 : 3′-dimethoxy-4 : 4′-dibenzyloxydistyryl ketone, but was different from the distyryl ketone prepared in the usual manner (m. p. 155°). In all cases, much resinous material was formed; apparently the inter-condensation of styryl methyl ketones does not stop at the stage represented by equation (B), but continues to give a mixture of still more complex products. Such resinification of unsaturated ketones has already been considered by Borsche (*Ber.*, 1909, **42**, 4499), Giua (*Gazzetta*, 1925, **55**, 567), and especially by Herzog (*Z. angew. Chem.*, 1922, **35**, 465, 641; 1923, **36**, 471; *Chem.-Ztg.*, 1925, **49**, 119).

We next directed our attention to the action of piperidine upon styryl methyl ketones, expecting that this base would behave similarly to alkali, but would be milder in its action and possibly yield the primary additive compound (I). In all the cases we have investigated, however, much resinification took place, and we have been able to isolate solid products only in minute yields. These compounds are not true intermolecular condensation products, but dimerides of the styryl ketone, and from their saturated nature and absence of colour they must be regarded as *cyclo*butane derivatives (IV or V) analogous to that obtained by Stobbe (*J. pr. Chem.*, 1912, **86**, 248; Stobbe and Hensel, *Ber.*, 1926, **59**, 2254)

(IV.)



$$\begin{array}{l} R\cdot\underset{|}{C}H\cdot\underset{|}{C}H\cdot COMe \\ R\cdot CH\cdot CH\cdot COMe \end{array}$$

$$\begin{array}{r} R\cdot\underset{|}{C}H\cdot\underset{|}{C}H\cdot COMe \\ COMe\cdot CH\cdot CHR \end{array}$$

(V.)

$[R = C_6H_3(OMe)_2]$

from phenyl 4-methoxystyryl ketone by the same method, and also to the compounds he and other workers have obtained by photopolymerisation (compare Stobbe and Hensel, *loc. cit.*).

Wieland (*Ber.*, 1904, **37**, 1145) obtained a dimeric form of phenyl styryl ketone by treating it with acetic anhydride containing a trace of sulphuric acid; but, applied to our compounds, this method yielded resinous material only, from which no pure substance has been isolated.

EXPERIMENTAL.

3 : 4-Dimethoxystyryl methyl ketone was prepared by Kaufmann and Radosević's method (*loc. cit.*) and found to melt at 85—86°, as given by Ryan and Plunkett (*loc. cit.*). The ketone can also be obtained in quantitative yield by the methylation of 3-methoxy-4-hydroxystyryl methyl ketone by Dickinson's method (J., 1926, 2234) for the preparation of 2-methoxystyryl benzyl ketone (Found : *M*,* 234, 207, 203. $C_{12}H_{14}O_3$ requires *M*, 206).

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* The molecular weights recorded in this paper were all determined ebullioscopically in chloroform by Menzies's method (Menzies and Wright, *J. Amer. Chem. Soc.*, 1921, **43**, 2314).

The *semicarbazone*, prepared by the usual method, crystallises from alcohol in colourless needles, m. p. 205°, which exhibit phototropic properties, becoming sulphur-yellow on short exposure to light. Crystallised from 50% acetic acid, it forms canary-yellow needles melting indefinitely about 180°. This is probably an unstable acetate, for on treatment with water or on keeping over potash it loses its crystalline form and colour, becoming identical with the original semicarbazone (Found: N, 16·1. $C_{13}H_{17}O_3N_3$ requires N, 16·0%).

3 : 3′ : 4 : 4′-Tetramethoxydistyryl ketone was obtained in fair yield by the direct alkaline condensation of veratraldehyde with acetone according to Stobbe and Haertel's method (*loc. cit.*). It was also readily prepared by condensation of 3 : 4-dimethoxystyryl methyl ketone (1·3 g.) with veratraldehyde (1 g.) in alcoholic solution (20 c.c.) in presence of dilute aqueous sodium hydroxide (3 c.c. of 8%); after a few hours, the yellow precipitate was collected and crystallised from alcohol, yielding the pure product, m. p. 84°. A peculiar property of this distyryl ketone was noted: a specimen which had been kept in a sealed tube for several months changed in colour, the golden-yellow crystals becoming yellowish-brown, and crumbled to a powder. The change appeared to start at various centres and slowly spread into the surrounding material, but complete conversion was never attained. The *tetrabromide*, prepared by treating the ketone in chloroform solution with the calculated amount of bromine, crystallised from benzene in colourless needles which darkened at 145° and melted at 152° with inflation [Found: Br, 47·3 (Stepanoff). $C_{21}H_{22}O_5Br_4$ requires Br, 47·4%].

Ethyl 3-mp-*Dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ⁵-cyclo*hexen*-1-*one*-2-*carboxylate* (III).—A solution of 3 : 3′ : 4 : 4′-tetramethoxydistyryl ketone (10 g.) and ethyl acetoacetate (4 g.) in boiling alcohol (75 c.c.) was treated with sodium ethoxide (0·4 g. of sodium in 25 c.c. of alcohol) and maintained at the boiling point for 5 minutes. The crystalline solid which separated on cooling (yield, above 90%) was twice recrystallised from absolute alcohol, in which it was sparingly soluble, giving bright yellow needles, m. p. 160—161° (Found: C, 69·3; H, 6·5. $C_{27}H_{30}O_7$ requires C, 69·5; H, 6·4%).

3-mp-*Dimethoxyphenyl*-5-mp-*dimethoxystyryl*-Δ⁵-cyclo*hexen*-1-*one* (II).—The above-mentioned ester (5 g.), dissolved in glacial acetic acid (75 c.c.), was boiled with 20% sulphuric acid (50 c.c.) under reflux for 4 hours. After cooling, the dark red liquid was slowly poured into ice-water (1000 c.c.). The greenish-yellow, curdy precipitate was crystallised from alcohol and then twice from ethyl acetate. The cyclo*hexenone* formed minute, pale yellow needles, m. p. 168°, which tenaciously retained traces of ethyl acetate. For analysis, the substance was heated in a vacuum at 100° for several hours. It readily absorbed two molecules of bromine, but no pure bromo-derivative could be isolated (Found: C, 73·0; H, 6·4. $C_{24}H_{26}O_5$ requires C, 73·1; H, 6·6%).

The direct preparation of 3-*mp*-dimethoxyphenyl-5-*mp*-dimethoxystyryl-Δ^5-*cyclo*hexen-1-one was carried out by the following modification of Francesconi and Cusmano's method (*loc. cit.*). Veratraldehyde (12 g.), dissolved in aqueous acetone (70 c.c.), was treated with sodium hydroxide solution (25 c.c. of 1%). After the mixture had been kept for 2 days in the ice-chest, the solid was separated and twice recrystallised from ethyl acetate; the pure product, m. p. 168°, was then obtained (yield 20%). The filtrate gave on dilution a viscous yellow oil, from which a small quantity of the normal monostyryl ketone (m. p. 85°) was isolated. The compound, m. p. 168°, gave no depression in melting point in admixture with the *cyclo*hexenone prepared as described above, the constitution of which is definitely determined. The *cyclo*hexenone was also prepared by keeping an acetone solution of 3 : 4-dimethoxystyryl methyl ketone, mixed with a few drops of 8% sodium hydroxide solution, at room temperature for several days. The solution slowly darkened and deposited a crystalline, yellow mass which, after recrystallisation from ethyl acetate, was identical with the Francesconi compound (Found: C, 73·1; H, 6·6%; *M*, 396, 395). Both substances were mixed with the synthesised *cyclo*hexenone (II), but no depression in melting point was noted.

Preparation of the cyclo*hexenone semicarbazone.* A solution of the *cyclo*hexenone (2 g.) in glacial acetic acid was treated with semicarbazide acetate. The yellow solution slowly became red and after 3 days the separated solid was filtered off, washed with water, and dried. On boiling with alcohol part dissolved and part was converted into a golden-yellow, crystalline powder; an identical product was obtained from the alcoholic solution. The *monosemicarbazone* forms golden-yellow rhombs, m. p. 226—227° to a red liquid, and regenerates the *cyclo*hexenone on being refluxed with aqueous-alcoholic oxalic acid for several hours (Found: N, 9·2. $C_{25}H_{29}O_5N_3$ requires N, 9·3%).

Dimeride of 3 : 4-*Dimethoxystyryl Methyl Ketone.*—3 : 4-Dimethoxystyryl methyl ketone (20 g.) was heated on a steam-bath with piperidine (30 c.c.) for 24 hours. The solution was diluted with water and acidified, and the resinous precipitate obtained, on repeated treatment with boiling alcohol, yielded a white, amorphous powder. For analysis, the compound, which was obtained only in very small yield, was precipitated from benzene solution by the gradual addition of light petroleum; m. p. 209—210° (Found: C, 70·2; H, 6·7; *M*, 418. $C_{24}H_{28}O_6$ requires C, 69·9; H, 6·8%; *M*, 412).

3-*Methoxy*-4-*ethoxystyryl Methyl Ketone.*—Ethylvanillin (5 g.), prepared according to Tiemann's method (*Ber.*, 1875, **8**, 1129), was dissolved in alcohol (5 c.c.) and acetone (15 c.c.) and treated with 1% sodium hydroxide solution (20 c.c.). After an hour, a yellow oil commenced to separate which only very slowly became solid. In subsequent experiments, seeding the mixture at this stage brought about a rapid separation of the solid ketone. Recrystallised from dilute alcohol, it formed yellow needles, m. p. 106° (yield, 83%). The ketone was also obtained in a colourless modification having the same melting point by allowing the yellow modification to stand in suspension in water or xylene for several weeks in direct sunlight. Whereas the yellow form gives an intense crimson coloration in concentrated hydrochloric acid, the colourless isomeride dissolves to a yellow solution (Found: C, 70·7; H, 7·0; *M*, 236. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%; *M*, 220). The *semicarbazone* separates from alcohol in pale yellow plates, m. p. 208—209° (Found: N, 15·4. $C_{14}H_{19}O_3N_3$ requires N, 15·2%).

3 : 3′-*Dimethoxy*-4 : 4′-*diethoxydistyryl Ketone.*—Ethylvanillin (5 g.) and acetone (1 c.c.) were dissolved in 50% alcohol (100 c.c.) together with 10% sodium hydroxide solution (2·5 c.c.) and the mixture was left at room temperature for 24 hours. The yellow precipitate was recrystallised from alcohol, the pure *ketone* separating in yellow needles, m. p. 123—124° (yield, 50%) (Found: C, 72·0; H, 6·8. $C_{23}H_{26}O_5$ requires C, 72·2; H, 6·8%).

Dimeride of 3-*Methoxy*-4-*ethoxystyryl Methyl Ketone.*—The styryl ketone (19 g.) was refluxed on a steam-bath with piperidine (30 c.c.) for 24 hours. The gummy precipitate formed on addition of water was repeatedly washed with alcohol, whereby resinous impurities were wholly removed. The polymeride was purified by slow precipitation from benzene solution by means of light petroleum. It formed a white, amorphous powder, m. p. 187° (yield, 5%) (Found: C, 70·9; H, 7·4; *M*, 446, 465. $C_{26}H_{32}O_6$ requires C, 70·9; H, 7·3%; *M*, 440).

Propylvanillin.—A mixture containing the potassium salt of vanillin (19 g.), propyl iodide (25 g.), and absolute alcohol (20 c.c.) was heated for 12 hours under reflux on the water-bath. After removal of part of the alcohol, the residue was poured into water; the precipitated oil rapidly solidified. This was dissolved in ether and repeatedly washed with dilute alkali solution to remove unchanged vanillin. The residue left after removal of the ether was recrystallised from dilute alcohol, *propylvanillin* being obtained in colourless crystals, m. p. 59—60° (yield, 60%) (Found: C, 67·8; H, 7·4. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%). The *semicarbazone* separated from alcohol in colourless needles, m. p. 156° (Found: N, 16·9. $C_{12}H_{17}O_3N_3$ requires N, 16·7%).

3-*Methoxy*-4-*propoxystyryl Methyl Ketone*.—A solution of propylvanillin (2 g.) in acetone (8 c.c.) and alcohol (3 c.c.) was treated with 1% aqueous sodium hydroxide (8 c.c.). The product, which rapidly separated, was twice recrystallised from alcohol, the pure styryl ketone forming bright yellow rhombs, m. p. 92—93° (Found: C, 71·9; H, 7·8. $C_{14}H_{18}O_3$ requires C, 71·8; H, 7·7%).

3-m-*Methoxy*-p-*propoxyphenyl*-5-m-*methoxy*-p-*propoxystyryl*-Δ^5-cyclo*hexen*-1-*one*.—The ketone (10 g.) in acetone (75 c.c.), alcohol (50 c.c.), and water (100 c.c.) was treated with 2*N*-sodium hydroxide (10 c.c.), and the whole left at room temperature for 3 days. The small amount of yellow precipitate crystallised from ethyl acetate in pale yellow needles, m. p. 152—153°. It readily absorbed two molecules of bromine, halochromic colour effects being shown, but no solid tetrabromide could be isolated (Found: C, 74·5; H, 7·6. $C_{28}H_{34}O_5$ requires C, 74·7; H, 7·6%).

iso*Propylvanillin*, prepared in the same way as the *n*-isomeride, formed a pale yellow, viscous liquid, b. p. 150—152°/13 mm. The *semicarbazone* separated from alcohol in colourless needles, m. p. 151—152° (Found: N, 16·6. $C_{12}H_{17}O_3N_3$ requires N, 16·7%).

3-*Methoxy*-4-iso*propoxystyryl methyl ketone*, prepared by the method described for the *n*-isomeride, separated as a yellow oil which only became solid after long standing. It crystallised from aqueous alcohol in yellow flakes, m. p. 51—53°. An acetone–alcoholic solution of the ketone in presence of alkali darkened fairly rapidly, but only resinous material was isolated. The *semicarbazone* formed yellow needles, m. p. 203—204° (Found: N, 14·6. $C_{15}H_{21}O_3N_3$ requires N, 14·4%).

Benzylvanillin, previously prepared by the oxidation of benzyl*iso*eugenol (Boehringer und Söhne, D.R.-P. 65,937, 1891), is more conveniently prepared by the following method. A thin alcoholic paste of the potassium salt of vanillin (23 g.) was heated under reflux with benzyl chloride (25 g.) for 12 hours. The excess of benzyl chloride was removed by short distillation in steam and the residual oil, which solidified on cooling, was twice recrystallised from alcohol, benzylvanillin being obtained in colourless crystals, m. p. 64—65° (yield, 70%).

3-*Methoxy*-4-*benzyloxystyryl Methyl Ketone*.—A solution of benzylvanillin (5 g.) in acetone (8 c.c.) and alcohol (20 c.c.) was treated with sodium hydroxide solution (8 c.c. of 0·5%) and kept in the ice-chest; an oil then separated which slowly solidified. The crude product (yield, 80%) contained a small amount of the corresponding distyryl ketone, which was only separated with difficulty by fractional crystallisation either from alcohol or ethyl acetate. The *ketone* crystallised from alcohol in yellow needles, m. p. 93° (Found: C, 76·4; H, 6·4; *M*, 280, 285. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%; *M*, 282). The *semicarbazone* formed a yellow powder, m. p. 200—201° (Found: N, 12·4. $C_{19}H_{21}O_3N_3$ requires N, 12·4%).

3 : 3′-*Dimethoxy*-4 : 4′-*dibenzyloxydistyryl Ketone*.—A solution of benzylvanillin (2 g.) in acetone (0·5 c.c.) and alcohol (30 c.c.) was treated with 1% sodium hydroxide solution (10 c.c.). After 24 hours, the mixture was neutralised with dilute acetic acid, whereupon an oil separated which rapidly solidified. The distyryl ketone crystallised from ethyl acetate in golden-yellow needles, m. p. 155°. Alternatively, the same compound may be obtained by condensation of 3-methoxy-4-benzyloxystyryl methyl ketone with benzylvanillin (Found: C, 78·1; H, 6·0. $C_{33}H_{30}O_5$ requires C, 78·3; H, 5·9%). The *tetrabromide*, obtained by treating the ketone in chloroform solution with the calculated amount of bromine, formed minute, colourless needles, m. p. 141° (decomp.), from benzene. This compound rapidly decomposes with loss of bromine.

An apparent isomeride of this distyryl ketone was isolated in an attempt to prepare the *cyclo*hexenone from 3-methoxy-4-benzyloxystyryl methyl ketone by the action of alkali in the following manner. The monostyryl ketone (10 g.) in acetone (36 c.c.) and alcohol (36 c.c.) was treated with 8% sodium hydroxide solution (25 c.c.), and the mixture was kept at room temperature for 6 hours and in the ice-chest for 2 days. A solid separated which, after three recrystallisations from ethyl acetate, was obtained in dark orange-yellow needles, m. p. 174—175°. This substance absorbs 2 molecules of bromine, but no solid bromide could be isolated (Found: C, 78·3; H, 6·2%).

Phenyl 3 : 4-*Dimethoxystyryl Ketone*.—A solution of veratraldehyde (5·6 g.) and acetophenone (4 g.) in alcohol (30 c.c.) was treated with 10% sodium hydroxide solution (12 c.c.). After an hour, an oil separated which slowly solidified; in subsequent experiments, seeding of the oil brought about almost instantaneous solidification. The chalkone separated from aqueous alcohol in yellow needles, m. p. 88° (yield, 70%) (Found: C, 75·9; H, 6·3. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%). Attempts to condense this compound to a *cyclo*hexenone by means of alkali failed, only resinous material being formed.

In conclusion, we desire to express our thanks to the Council of the Department of Scientific and Industrial Research for a grant to one of us (R. D.) and also to the Cumberland County Council for the renewal of a scholarship (F. I.) which has enabled this research to be carried out.

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