187. *Condensation of Diketones with Aromatic Compounds. Part I. α-Diketones and Veratrole.*

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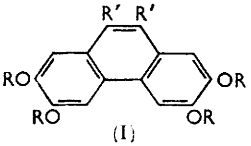
α-Diketones react with veratrole in sulphuric acid to form 9,10-disubstituted 2,3,6,7-tetramethoxyphenanthrenes.

The reaction of veratrole with α-diketones in 70% v/v aqueous sulphuric acid was examined some years ago in this Department by Drs. A. M. Meston and J. M. C. Thompson.[1] They observed that biacetyl gave a substance $C_{20}H_{22}O_4$, m. p. 224°, and that bipropionyl gave the corresponding substance $C_{22}H_{26}O_4$, m. p. 181—182°, but they did not assign structures to these products. We have now investigated this reaction further.

The veratrole–biacetyl product, for which we have confirmed the formula $C_{20}H_{22}O_4$, is best obtained by using 80% v/v aqueous sulphuric acid. It contains four methoxyl groups, has the characteristic ultraviolet absorption of a polycyclic aromatic system, and was shown to be the tetramethoxydimethylphenanthrene (I; $R = R' = Me$) in the following manner. Demethylation by boron tribromide gave the tetrahydroxy-compound (I; $R = H$, $R' = Me$) which on acetylation afforded the tetra-acetate (I; $R = Ac$, $R' = Me$). The latter possesses ultraviolet absorption resembling that of a polyalkylphenanthrene[2] (the acetoxyl and the methyl group have comparable effects[3] on the ultraviolet absorption of an aromatic system). In addition, the ultraviolet absorption of the original veratrole–biacetyl product is in excellent agreement with that of the diacetoxytetramethoxyphenanthrene (I;



(I)

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[1] Meston, Ph.D. Thesis, Aberdeen, 1952, p. 47.

[2] Heilbronner, Däniker, and Plattner, *Helv. Chim. Acta*, 1949, **32**, 1723.

[3] Ramart-Lucas, Matti, and Guilmart, *Bull. Soc. chim. France*, 1948, 1215; Musgrave, *J.*, 1957, 1104; cf. Brockmann and Budde, *Chem. Ber.*, 1953, **86**, 432.

R = Me, R′ = OAc) which resulted from the reductive acetylation of 2,3,6,7-tetramethoxyphenanthraquinone. At this point in our investigation a synthesis of 2,3,6,7-tetramethoxy-9,10-dimethylphenanthrene was published by Govindachari *et al.*[4] and a specimen obtained by their route proved identical with the veratrole–biacetyl product.

The compounds obtained from the reactions of bipropionyl,[1] cyclohexane-1,2-dione, and benzil with veratrole in sulphuric acid have ultraviolet absorptions similar to that of the tetramethoxydimethylphenanthrene (I; R = R′ = Me) and consequently they are, respectively, the 9,10-diethyl (I; R = Me, R′ = Et), the 9,10-tetramethylene (I; R = Me, R′ + R′ = $[CH_2]_4$), and the 9,10-diphenyl (I; R = Me, R′ = Ph) analogues. Condensation of veratrole with biacetyl probably takes place by way of 2,3-bis-(3,4-dimethoxyphenyl)butane-2,3-diol as this is also converted into the tetramethoxydimethylphenanthrene (I; R = R′ = Me) by sulphuric acid. The reaction of glyoxal sulphate with veratrole in sulphuric acid fails to yield a phenanthrene derivative, giving instead 1,1,2,2-tetrakis-(3,4-dimethoxyphenyl)ethane which has previously been obtained by using the glyoxal sodium bisulphite compound under similar conditions.[5]

EXPERIMENTAL

Ultraviolet absorption spectra were determined for ethanolic solutions by using a Unicam S.P. 500 or a Hilger " Ultrascan " spectrophotometer.

Reaction of Veratrole and Biacetyl.—To a solution of veratrole (25 g.) in 80% v/v aqueous sulphuric acid (300 ml.) biacetyl (7·8 g.) was added dropwise with stirring during ½ hr. The permanganate-coloured mixture was kept at room temperature for 18 days, then filtered, and the solid was washed with water and dried. Crystallisation from benzene (charcoal) and then from ethanol gave 2,3,6,7-tetramethoxy-9,10-dimethylphenanthrene (17·2 g., 58%) as needles, m. p. 222—223° (Found: C, 73·4; H, 6·9; OMe, 42·0. Calc. for $C_{20}H_{22}O_4$: C, 73·6; H, 6·8; 4OMe, 38·05%), $\lambda_{max.}$ 2230 (log ε 4·343), 2380 (log ε 4·413), 2575 (log ε 4·894), 2885 (log ε 4·593), 3040 (log ε 4·304), 3400 (log ε 3·177), and 3570 Å (log ε 2·823), $\lambda_{infl.}$ 2500 (log ε 4·684) and 3240 Å (log ε 3·260). The use of different concentrations of sulphuric acid gave lower yields: 65% v/v, 0%; 70% v/v, 2—36%; 75% v/v, 48%; 85% v/v, 0%. The m. p. of the phenanthrene was not depressed on admixture with an authentic specimen, m. p. 222—223°, prepared by the method of Govindachari *et al.*[4] and the infrared and the ultraviolet absorption spectra of the two preparations were identical. The *picrate*, which separated from hot benzene solutions, crystallised from ethanol in reddish-brown needles, m. p. 175·5—176° (Found: C, 56·3; H, 4·6; N, 7·4. $C_{20}H_{22}O_4,C_6H_3N_3O_7$ requires C, 56·2; H, 4·55; N, 7·55%).

2,3,6,7-*Tetrahydroxy*-9,10-*dimethylphenanthrene*.—Boron tribromide (6 ml.) was added dropwise to a hot solution of 2,3,6,7-tetramethoxy-9,10-dimethylphenanthrene (5 g.) in dry benzene (200 ml.). The mixture was heated under reflux for 3 hr., poured into water, and extracted with ether. The ethereal solution was washed with 2N-sodium hydroxide solution (2 × 100 ml.) which, on acidification with concentrated hydrochloric acid, yielded the *hydroxyphenanthrene* which crystallised from glacial acetic acid (charcoal) in needles (3·8 g.), m. p. (evacuated Pyrex capillary) 309—310° (with darkening above 260°) (Found: C, 71·3; H, 5·3. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%).

2,3,6,7-*Tetra-acetoxy*-9,10-*dimethylphenanthrene*.—A mixture of 2,3,6,7-tetrahydroxy-9,10-dimethylphenanthrene (0·5 g.), anhydrous sodium acetate (0·05 g.), and acetic anhydride (10 ml.) was heated under reflux for 9 hr. The solid which separated on cooling crystallised from glacial acetic acid, giving the *acetoxyphenanthrene* as needles (0·55 g.), m. p. 247—248° (Found: C, 65·7; H, 5·1; Ac, 38·4. $C_{24}H_{22}O_8$ requires C, 65·75; H, 5·05; 4Ac, 39·2%), $\lambda_{max.}$ 2270 (log ε 3·840), 2585 (log ε 4·810), 2785 (log ε 4·562), 3025 (log ε 4·085), 3415 (log ε 2·837), and 3570 Å (log ε 2·670), $\lambda_{infl.}$ 2370 (log ε 3·910), 2510 (log ε 4·663), 2840 (log ε 4·442), and 3235 Å (log ε 2·872).

Dehydration of 2,3-*Bis*-(3,4-*dimethoxyphenyl*)*butane*-2,3-*diol*.—Reduction of 3,4-dimethoxyacetophenone by amalgamated aluminium by the procedure of Sisido and Nozaki[6] gave 2,3-bis-(3,4-dimethoxyphenyl)butane-2,3-diol, m. p. 165—167° (lit.,[7] m. p. 169°), in 80% yield. A

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[4] Govindachari, Lakshmikantham, Pai, and Rajappa, *Tetrahedron*, 1960, **9**, 53.

[5] Robinson, *J.*, 1915, **107**, 267.

[6] Sisido and Nozaki, *J. Amer. Chem. Soc.*, 1948, **70**, 776.

[7] Mannich, *Arch. Pharm.*, 1910, **248**, 139.

mixture of the diol (0·8 g.) and 75% v/v aqueous sulphuric acid (100 ml.) was kept at room temperature for 7 days and then filtered. The solid was washed with water, dried, and crystallised from benzene (charcoal), giving 2,3,6,7-tetramethoxy-9,10-dimethylphenanthrene as needles (0·3 g.), m. p. and mixed m. p. 222—223°. The infrared and ultraviolet absorption spectra were identical with those of the authentic specimen.

9,10-*Diethyl*-2,3,6,7-*tetramethoxyphenanthrene*.[1]—This had m. p. 181—182°, $\lambda_{\text{max.}}$ 2575 (log ε 4·877) and 2885 Å (log ε 4·574), $\lambda_{\text{infl.}}$ 2260 (log ε 4·273), 2390 (log ε 4·426), 2505 (log ε 4·690), 3025 (log ε 4·291), and 3110 Å (log ε 4·000).

1,2,3,4-*Tetrahydro*-6,7,10,11-*tetramethoxytriphenylene*.—Cyclohexane-1,2-dione (10 g.) was added in portions, with stirring, to a solution of veratrole (25 g.) in 80% v/v aqueous sulphuric acid (300 ml.). The mixture was stirred for ½ hr. and kept at room temperature for 20 days. The solid obtained by filtration was washed with water, dried, and crystallised from benzene (charcoal) and then from ethanol, giving the *phenylene derivative* (2·1 g.) as needles, m. p. 234—234·5° (Found: C, 74·8; H, 6·9. $C_{22}H_{24}O_4$ requires C, 74·95; H, 6·85%), $\lambda_{\text{max.}}$ 2230 (log ε 4·321), 2390 (log ε 4·429), 2575 (log ε 4·881), 2890 (log ε 4·580), 3030 (log ε 4·321), 3230 (log ε 3·293), 3380 (log ε 3·231), and 3550 Å (log ε 2·895), $\lambda_{\text{infl.}}$ 2500 (log ε 4·661) and 2840 Å (log ε 4·515).

2,3,6,7-*Tetramethoxy*-9,10-*diphenylphenanthrene*.—Aqueous sulphuric acid (80% v/v; 300 ml.) was added with stirring to a suspension of benzil (19 g.) in veratrole (25 g.). The mixture was stirred for ½ hr. and then kept at room temperature for 7 weeks. The solid obtained by filtration was washed with water and with methanol. Crystallisation from benzene (charcoal) and then from ethanol gave the *phenylphenanthrene* (2·9 g.) as needles, m. p. 231·5—232·5° (Found: C, 80·1; H, 6·0. $C_{30}H_{26}O_4$ requires C, 80·0; H, 5·8%), $\lambda_{\text{max.}}$ 2200 (log ε 4·536), 2620 (log ε 4·800), 2880 (log ε 4·682), 3415 (log ε 3·291), and 3580 Å (log ε 3·022), $\lambda_{\text{infl.}}$ 2375 (log ε 4·472), 2540 (log ε 4·695), 3020 (log ε 4·330), and 3150 Å (log ε 3·965).

9,10-*Diacetoxy*-2,3,6,7-*tetramethoxyphenanthrene*.—A mixture of 2,3,6,7-tetramethoxyphenanthraquinone [8] (1·0 g.), zinc dust (1·0 g.), anhydrous sodium acetate (0·2 g.), and acetic anhydride (20 ml.) was heated under reflux for 2·5 hr. and added to water (600 ml.). The solid which separated was collected, washed with water, dried, and crystallised from benzene. The *acetoxyphenanthrene* (1·1 g.) separated as prisms, m. p. 240—241° (Found: C, 63·8; H, 5·3; Ac, 20·2. $C_{22}H_{22}O_8$ requires C, 63·75; H, 5·35; 2Ac, 20·75%), $\lambda_{\text{max.}}$ 2215 (log ε 4·343), 2570 (log ε 4·927), 2850 (log ε 4·603), 3380 (log ε 3·331), and 3550 Å (log ε 3·046), $\lambda_{\text{infl.}}$ 2395 (log ε 4·462), 2490 (log ε 4·696), 2995 (log ε 4·306), 3100 (log ε 3·971), and 3220 Å (log ε 3·391).

1,1,2,2-*Tetrakis*-(3,4-*dimethoxyphenyl*)*ethane*.—Glyoxal sulphate [9] (20 g.) was added in portions, with stirring, to a solution of veratrole (25 g.) in 70% v/v aqueous sulphuric acid (300 ml.). The mixture was shaken for 6 days, kept for a further 6 days, and filtered. The resulting solid (16 g.) was washed with water, dried, and crystallised from benzene (charcoal), giving 1,1,2,2-tetrakis-(3,4-dimethoxyphenyl)ethane as prisms, m. p. 148—150° (lit.,[5] m. p. 148°) (Found: C, 70·7; H, 6·7; OMe, 44·3. Calc. for $C_{34}H_{38}O_8$: C, 71·05; H, 6·65; 8OMe, 43·2%), $\lambda_{\text{max.}}$ 2820 Å (log ε 4·096), $\lambda_{\text{infl.}}$ 2325 (log ε 4·443) and 2880 Å (log ε 4·055).

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[8] Oliverio, *Rend. Semin. Fac. Sci. R. Univ. Cagliari*, 1934, **4**, 126.

[9] Raudnitz, *J.*, 1948, 763.