558. *Condensation of Diketones with Aromatic Compounds. Part III.*[1] *Further Reactions of α-Diketones*

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The acid-catalysed reactions of biacetyl with catechol, *m*-dimethoxybenzene, or 1,2,4-trimethoxybenzene, give 3,3-diarylbutan-2-ones. Veratrole reacts with acenaphthenequinone in a similar manner to give 2,2-bis-(3,4-dimethoxyphenyl)acenaphthenone but with 9,10-phenanthrenequinone it gives 2,3,6,7-tetramethoxyphenanthro[9,10-*l*]phenanthrene.

In Part I [2] we described the condensation of α-diketones with veratrole in sulphuric acid to give 9,10-disubstituted 2,3,6,7-tetramethoxyphenanthrenes. We have now examined the products formed in some related reactions.

The reaction between biacetyl and catechol in " 70% " aqueous sulphuric acid was reported by Niederl and Nagel [3] to give a compound $C_{16}H_{14}O_4$, m. p. 300°, in unspecified yield, which they claimed to be a tetrahydroxyindanoindane. An attempt by Meston [4]

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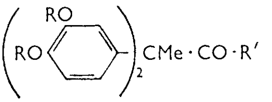
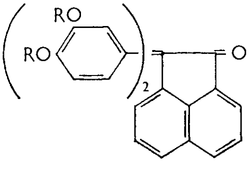
[1] Part II, I. M. Davidson and O. C. Musgrave, *J.*, 1963, 3154.
[2] D. L. Manson and O. C. Musgrave, *J.*, 1963, 1011.
[3] J. B. Niederl and R. H. Nagel, *J. Amer. Chem. Soc.*, 1940, **62**, 3070.
[4] A. M. Meston, Ph.D. Thesis, Aberdeen, 1952, p. 45.

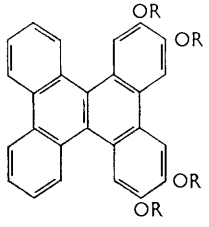
to repeat this work was unsuccessful and we also have been unable to obtain this product despite the use of concentrations of sulphuric acid ranging from 70% w/v to 85% v/v. The reactions in the more concentrated aqueous sulphuric acid solutions (65—85% v/v) afforded an intractable blue-black solid product which could not be purified. The use of somewhat lower concentrations of sulphuric acid either in water or in aqueous acetic acid resulted in the formation of a compound $C_{16}H_{18}O_6$. The infrared spectral absorption of this indicates the presence of hydroxyl and carbonyl groups while the ultraviolet absorption is similar to that [5] of 4-methylcatechol. We formulate the compound accordingly as the monohydrate of 3,3-bis-(3,4-dihydroxyphenyl)butan-2-one (I; R = H, R′ = Me).



(I)



(II)



(III)

Acetylation gave the corresponding tetra-acetoxy-ketone (I; R = Ac, R′ = Me) which, however, on treatment with methanolic sodium hydroxide solution followed by acidification gave acetic acid corresponding to *five* acetyl groups. This high value is attributed to the splitting off of the *C*-acetyl group as cleavage of the parent unsubstituted compound, 3,3-diphenylbutan-2-one,[6] is also found to occur to some extent (Found: Ac, 2·3%) under similar conditions. The attack by hydroxide ion on the *C*-acetyl carbonyl groups in these compounds is presumably facilitated by the inductive electron-withdrawal effects of the aromatic rings. Methylation of the tetrahydroxy-ketone (I; R = H, R′ = Me) gave the corresponding tetramethoxy-ketone the structure of which was proved by the following alternative synthesis. Condensation of veratrole with pyruvic acid in concentrated sulphuric acid gave the tetramethoxy-acid (I; R = Me, R′ = OH). The acid chloride obtained from this reacted with the magnesium derivative of diethyl malonate to give a product which on hydrolysis and decarboxylation afforded the desired tetramethoxy-ketone (I; R = R′ = Me). Both the latter and the corresponding tetra-acetoxy-ketone show the expected light absorption. The tetramethoxy-ketone was not converted into 2,3,6,7-tetramethoxy-9,10-dimethylphenanthrene by the action of 75% v/v aqueous sulphuric acid showing that it is not an intermediate in the condensation [2] which occurs between veratrole and biacetyl under these conditions.

The reactions of biacetyl with *m*-dimethoxybenzene (in 70% v/v aqueous sulphuric acid) and with 1,2,4-trimethoxybenzene (in polyphosphoric acid) gave the compounds $C_{20}H_{24}O_5$ and $C_{22}H_{28}O_7,\frac{1}{2}H_2O$, respectively. The light absorption of these products indicates that they also are 3,3-diarylbutan-2-ones.

From the condensation of acenaphthenequinone with catechol in acetic acid–sulphuric acid, Matei [7] obtained a product, m. p. 250—270°, which he suggested was the tetrahydroxy-ketone (II; R = H). By performing the reaction in 70% v/v aqueous sulphuric acid we obtained a product, m. p. 270—271°, the ultraviolet absorption of which closely resembles that of a mixture of 2,2-diphenylacenaphthenone [8] (1 mole) and 4-methylcatechol [5] (2 moles) and confirms that Matei's formulation is correct. The product formed a tetra-acetate, m. p. 97—98°, as did Matei's compound, and on methylation gave the tetramethoxy-ketone (II; R = Me) which could also be obtained by the reaction of acenaphthenequinone with veratrole in sulphuric acid.

The reaction between phenanthrene-9,10-quinone and veratrole in 70% v/v sulphuric

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[5] L. Barker and N. W. Hollingworth, *J. Appl. Chem.*, 1959, **9**, 16.

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

[7] I. Matei, *Ber.*, 1929, **62***B*, 2095.

[8] R. F. Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 428.

acid or in polyphosphoric acid took a different course. The product, $C_{30}H_{24}O_4$, does not contain a carbonyl group and because of the resemblance of its ultraviolet absorption to that of tetrabenzonaphthalene[9] is considered to be the 2,3,6,7-tetramethoxyphenanthrophenanthrene (III; R = Me). Catechol reacted with phenanthrene-9,10-quinone in a similar manner to give the corresponding tetrahydroxy-compound which we were unable to obtain pure. This on methylation gave the above tetramethoxy-compound and on acetylation afforded the 2,3,6,7-tetra-acetoxyphenanthrophenanthrene (III; R = Ac), the ultraviolet absorption of which resembles closely that of tetrabenzonaphthalene. The structure of the tetramethoxy-compound was confirmed by its alternative synthesis from 2,3,6,7-tetramethoxy-9,10-diphenylphenanthrene[2] which underwent a Scholl reaction[10] on treatment with aluminium chloride in nitrobenzene. The reactions of 1,2,4-trimethoxybenzene with acenaphthenequinone or with phenanthrene-9,10-quinone failed to give condensation products. Instead the quinones acted as hydrogen-acceptors and 2,2',4,4',5,5'-hexamethoxybiphenyl was formed.

EXPERIMENTAL

Ultraviolet spectra were measured for ethanolic solutions using a Hilger " Ultrascan " spectrophotometer. Infrared spectra were recorded for Nujol mulls with a Perkin-Elmer " Infracord " model 137 spectrophotometer.

Condensation of Biacetyl with Catechol.—Biacetyl (1·7 g.) was added with cooling and stirring to a solution of catechol (11 g.) in glacial acetic acid (35 ml.) and 70% v/v aqueous sulphuric acid (20 ml.). The mixture was warmed at 80° for 1 hr., kept for 24 hr., and diluted with water (50 ml.). Next day the solid was collected and crystallised from water (charcoal) giving 3,3-*bis*-(3,4-*dihydroxyphenyl*)*butan*-2-*one monohydrate* (4·3 g.) as needles, m. p. 141—142° (Found: C, 63·1; H, 5·8. $C_{16}H_{16}O_5,H_2O$ requires C, 62·75; H, 5·9%), $\lambda_{max.}$ 2850 Å (log ε 3·933), $\nu_{max.}$ 3350 (hydrogen-bonded OH) and 1680 cm.$^{-1}$ (hydrogen-bonded C=O). The same product (2·4 g.) was obtained when similar quantities of the reactants were kept for 2 weeks in 50% v/v aqueous sulphuric acid (50 ml.).

3,3-*Bis*-(3,4-*diacetoxyphenyl*)*butan*-2-*one*.—Acetylation of 3,3-bis-(3,4-dihydroxyphenyl)-butan-2-one monohydrate (0·5 g.) by heating under reflux for 3 hr. with anhydrous sodium acetate (0·3 g.) and acetic anhydride (15 ml.) gave the *bisdiacetoxy-ketone* (0·66 g.) which separated as needles from ethanol, m. p. 145—146° [Found: C, 63·0; H, 5·3; Ac, 46·4%; *M* (ebullioscopic in benzene), 488. $C_{24}H_{24}O_9$ requires C, 63·15; H, 5·3; 5 Ac, 47·1%; *M*, 456·45]; $\lambda_{max.}$ 2665 Å (log ε 3·199), 2720 (3·187), $\lambda_{infl.}$ 2880 Å (log ε 2·869), $\nu_{max.}$ 1765 (acetate C=O) and 1710 cm.$^{-1}$ (ketone C=O).

3,3-*Bis*-(3,4-*dimethoxyphenyl*)*butan*-2-*one*.—(*a*) Methylation of 3,3-bis-(3,4-dihydroxyphenyl)-butan-2-one monohydrate (0·5 g.) by heating under reflux with anhydrous potassium carbonate (3·0 g.), dry acetone (20 ml.), and dimethyl sulphate (5 ml.) for 6 hr. gave the *bisdimethoxy-ketone* (0·61 g.) as plates from methanol, m. p. 83·5—84·5° (Found: C, 69·7; H, 6·9; MeO, 36·6. $C_{20}H_{24}O_5$ requires C, 69·75; H, 7·0; 4 MeO, 36·05%); $\lambda_{max.}$ 2815 Å (log ε 3·814), $\lambda_{infl.}$ 2300 Å (log ε 4·206), $\nu_{max.}$ 1700 cm.$^{-1}$ (C=O).

(*b*) Veratrole (32 g.) was added to a solution of pyruvic acid (10 g.) in 90% v/v aqueous sulphuric acid (80 ml.) at between −5 and 0° during 1 hr. with stirring. The mixture was poured on to ice (500 g.) with vigorous stirring giving αα-*bis*-(3,4-*dimethoxyphenyl*)*propionic acid* which crystallised from methanol in plates (31 g.), m. p. 89—90° (Found: C, 65·6; H, 6·6. $C_{19}H_{22}O_6$ requires C, 65·9; H, 6·4%); $\lambda_{max.}$ 2805 Å (log ε 3·750), $\nu_{max.}$ 3300 (carboxyl OH) and 1725 cm.$^{-1}$ (carboxyl C=O).

A solution of diethyl malonate (2·4 g.) in ethanol (1 ml.) and dry benzene (5 ml.) was added during 30 min. to a mixture of magnesium turnings (0·36 g.), dry benzene (10 ml.), and ethanol (1 ml.), the reaction being initiated by the addition of a crystal of iodine. The mixture was heated under reflux until all the magnesium had dissolved and distilled until all the ethanol had been removed, giving a solution of the magnesium derivative of diethyl malonate.

αα-Bis-(3,4-dimethoxyphenyl)propionic acid (3·46 g.) was heated under reflux with methanol

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[9] K. F. Lang, H. Buffleb, and J. Kalowy, *Chem. Ber.*, 1961, **94**, 523.

[10] A. T. Balaban and C. D. Nenitzescu, " Friedel–Crafts and Related Reactions," ed. G. A. Olah, Interscience Publishers, New York, 1964, vol. II, p. 979.

(10 ml.) and sodium hydroxide (0·5 g.) for 2 hr. Filtration gave the sodium salt which was dried at 60°/10 mm. for 12 hr. A mixture of the sodium salt (2 g.), dry benzene (20 ml.), and pyridine (1 drop) was treated at between −5 and 0° with a solution of redistilled oxalyl chloride (5 ml.) in dry benzene (10 ml.). After gas evolution had ceased (5 min.) the mixture was evaporated at 10°/10 mm. Benzene (2 × 10 ml. portions) was added and evaporated to ensure removal of the excess of oxalyl chloride. The residue was dissolved in dry benzene and the solution was filtered and added with stirring and cooling during 30 min. to the solution of the magnesium derivative of diethyl malonate described above. The mixture was heated under reflux for 1 hr., added to ice (50 g.) and 2N-hydrochloric acid (50 ml.), and the organic layer washed with more 2N-hydrochloric acid, then with water, dried (Na_2SO_4), and evaporated under reduced pressure. The residual oil was heated under reflux for 2 hr. with glacial acetic acid (10 ml.), concentrated hydrochloric acid (10 ml.), and water (2 ml.). The mixture was diluted with water (50 ml.) and extracted thoroughly with ether. The extract was washed with sodium carbonate solution and then with water, dried (Na_2SO_4), and evaporated. The residue crystallised from methanol giving 3,3-bis-(3,4-dimethoxyphenyl)butan-2-one (0·17 g.), m. p. 83—84°, undepressed on admixture with the specimen prepared by method (*a*) above. The infrared spectra of the two specimens were identical.

3,3-*Bis*-(2,4-*dimethoxyphenyl*)*butan*-2-*one*.—Biacetyl (2 g.) was added to a solution of *m*-dimethoxybenzene (6·9 g.) in 70% v/v aqueous sulphuric acid (50 ml.) with cooling and stirring during 30 min. The mixture was kept for 14 days and then poured into water, and the resulting solid was crystallised from ethanol (charcoal) giving the *bisdimethoxy-ketone* (2·7 g.), m. p. 228—230° (Found: C, 69·7; H, 7·2; MeO, 36·0. $C_{20}H_{24}O_5$ requires C, 69·75; H, 7·0; 4 MeO, 36·05%), $\lambda_{max.}$ 2835 Å (log ε 3·781), $\nu_{max.}$ 1700 cm.$^{-1}$ (C=O). No product was obtained when polyphosphoric acid was used instead of sulphuric acid.

3,3-*Bis*-(2,4,5-*trimethoxyphenyl*)*butan*-2-*one*.—A mixture of 1,2,4-trimethoxybenzene (1·68 g.), biacetyl (0·43 g.), and polyphosphoric acid (15 g.) was heated at 60° for 30 min., poured on to crushed ice (50 g.), and extracted with ether. The extract was washed with sodium hydrogen carbonate solution and water, dried ($MgSO_4$), and evaporated. The residue crystallised from aqueous ethanol giving the *bistrimethoxy-ketone hemihydrate* (0·6 g.), m. p. 101—102° (Found: C, 63·9; H, 7·1; MeO, 45·7. $C_{22}H_{28}O_7,\frac{1}{2}H_2O$ requires C, 63·9; H, 7·05; 6 MeO, 45·05%), $\lambda_{max.}$ 2920 Å (log ε 4·006), $\nu_{max.}$ 1700 cm.$^{-1}$ (C=O).

2,2-*Bis*-(3,4-*dimethoxyphenyl*)*acenaphthenone*.—(*a*) Aqueous sulphuric acid (70% v/v, 50 ml.) was added to a stirred mixture of acenaphthenequinone (3·54 g.) and veratrole (6·9 g.). After 3 weeks the solid was collected and crystallised from ethanol to give the *acenaphthenone* (4·2 g.) as plates m. p. 130—131·5° (Found: C, 76·6; H, 5·6. $C_{28}H_{24}O_5$ requires C, 76·35; H, 5·5%); $\lambda_{max.}$ 2800 Å (log ε 3·864), 3190 (3·739), and 3460 (3·731), $\lambda_{infl.}$ 2360 Å (log ε 4·455) and 2550 (4·283), $\nu_{max.}$ 1720 cm.$^{-1}$ (C=O). The use of 75% v/v aqueous sulphuric acid gave a similar yield but little or no product resulted when higher concentrations were used. The same product resulted in 20% yield when polyphosphoric acid at 60° was used to effect the condensation.

(*b*) Acenaphthenequinone (4·5 g.) was added slowly to a solution of catechol (5·5 g.) in 70% v/v aqueous sulphuric acid (50 ml.). The mixture was heated to 50°, cooled, and the resulting solid was crystallised first from aqueous methanol and then from ethanol (charcoal) giving 2,2-bis-(3,4-dihydroxyphenyl)acenaphthenone (2·6 g.) as almost colourless needles, m. p. 270—271° (lit.,[7] 250—270°); $\lambda_{max.}$ 2850 Å (log ε 3·924), 3180 (3·732), and 3430 (3·708), $\lambda_{infl.}$ 2500 Å (log ε 4·255), $\nu_{max.}$ 3300 (hydrogen-bonded OH) and 1690 cm.$^{-1}$ (hydrogen-bonded C=O).

Methylation of this compound (0·3 g.) by heating under reflux with anhydrous potassium carbonate (1 g.), dimethyl sulphate (2 g.), and acetone (20 ml.) for 6 hr. gave 2,2-bis-(3,4-dimethoxyphenyl)acenaphthenone (0·32 g.), m. p. 131—131·5°, which crystallised from light petroleum (b. p. 80—100°). The m. p. was not depressed on admixture with a specimen prepared by method (*a*).

2,2-*Bis*-(3,4-*diacetoxyphenyl*)*acenaphthenone*.—Acetylation of 2,2-bis-(3,4-dihydroxyphenyl)-acenaphthenone (0·3 g.) by heating under reflux with anhydrous sodium acetate (0·3 g.) and acetic anhydride (20 ml.) gave 2,2-bis-(3,4-diacetoxyphenyl)acenaphthenone (0·4 g.) which crystallised from ethanol in needles, m. p. 97—98° (lit.,[7] 97—98°) (Found: C, 69·3; H, 4·4; Ac, 34·5. Calc. for $C_{32}H_{24}O_9$: C, 69·55; H, 4·4; 4 Ac, 31·15%); $\lambda_{max.}$ 2810 Å (log ε 4·033), 3125 (3·876), and 3470 (3·823), $\lambda_{infl.}$ 2560 Å (log ε 4·449).

2,3,6,7-*Tetramethoxyphenanthro*[9,10-*l*]*phenanthrene*.—(*a*) A mixture of phenanthrene-9,10-quinone (2·08 g.), veratrole (2·76 g.), and 70% v/v aqueous sulphuric acid (50 ml.) was stirred for

30 min., kept for 2 weeks, and filtered. The resulting solid was washed with water and crystallised from ethanol giving the *phenanthrophenanthrene* (1·8 g.), m. p. 150—151° (Found: C, 80·5; H, 5·1; MeO, 27·4. $C_{30}H_{24}O_4$ requires C, 80·35; H, 5·4; 4 MeO, 27·5%); $\lambda_{max.}$ 2260 Å (log ε 4·541), 2590 (4·808), 2850 (4·281), 3010 (4·220), 3330 (4·510), and 3630 (3·521), $\lambda_{infl.}$ 2520 Å (log ε 4·770) and 3250 (4·470). A similar yield was obtained by using 75% v/v aqueous sulphuric acid but the use of higher concentrations of the acid gave no product.

(*b*) A mixture of veratrole (2·76 g.), phenanthrene-9,10-quinone (2·08 g.), and polyphosphoric acid (20 g.) was heated at 60° with stirring for 30 min., cooled, and added to ice–water (50 ml.). The mixture was shaken with ether and the ethereal extract was washed with aqueous sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated. The residue crystallised from light petroleum (b. p. 80—100°) (charcoal) giving the 2,3,6,7-tetramethoxyphenanthrophenanthrene (0·54 g.) as plates, m. p. 150—151°. The m. p. was not depressed on admixture with the specimen prepared by method (*a*) and the infrared spectra of the two samples were identical.

(*c*) Phenanthrene-9,10-quinone (1 g.) was added with stirring to a solution of catechol (3 g.) in 70% v/v aqueous sulphuric acid (50 ml.). The mixture was stirred for 1 hr., kept for 7 days, and filtered giving crude 2,3,6,7-tetrahydroxyphenanthrophenanthrene (0·62 g.) as a dark green solid, m. p. 220—225° (with darkening about 170°); $\lambda_{max.}$ 2280 Å ($E^{1\%}_{1\,cm.}$ 780), 2615 (1195), 2860 (360), 3060 (330), and 3375 (550), $\lambda_{infl.}$ 3660 Å ($E^{1\%}_{1\,cm.}$ 85). Methylation of this product (0·3 g.) by heating under reflux for 3 hr. with anhydrous potassium carbonate (1·0 g.), dimethyl sulphate (2 g.), and acetone (20 ml.) gave the 2,3,6,7-tetramethoxyphenanthrophenanthrene (0·12 g.), m. p. 150—151° which crystallised from ethanol. The m. p. was not depressed on admixture with a specimen prepared by method (*a*); the infrared spectra of the two specimens were identical.

2,3,6,7-*Tetra-acetoxyphenanthro*[9,10-*l*]*phenanthrene*.—Acetylation of the crude 2,3,6,7-tetrahydroxyphenanthrophenanthrene (0·4 g.) by heating under reflux for 3 hr. with anhydrous sodium acetate (0·4 g.) and acetic anhydride (20 ml.) gave the *tetra-acetate* (0·42 g.), m. p. 251—252° (with darkening above 230°) which crystallised from aqueous acetic acid (Found: C, 72·8; H, 4·55; Ac, 34·0. $C_{34}H_{24}O_8$ requires C, 72·85; H, 4·3; 4 Ac, 30·7%); $\lambda_{max.}$ 2530 Å (log ε 4·781), 2980 (4·252), 3115 (4·355), 3240 (4·393), 3400 (3·801), and 3570 (3·718), $\lambda_{infl.}$ 2610 Å (log ε 4·703) and 2810 (4·278).

Cyclisation of 2,3,6,7-*Tetramethoxy*-9,10-*diphenylphenanthrene*.—Anhydrous aluminium chloride (7 g.) was added portionwise to a cooled solution of the phenanthrene [2] (0·75 g.) in nitrobenzene (30 ml.). The viscous mixture was kept overnight, heated for 3 hr. on the steam-bath, and added to a mixture of 4N-aqueous hydrochloric acid (100 ml.) and crushed ice (50 g.). The mixture was steam-distilled to remove the nitrobenzene and the residual liquid was extracted with ether. The extract was washed with aqueous sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated. Crystallisation of the residual solid from light petroleum (b. p. 80—100°) gave 2,3,6,7-tetramethoxyphenanthrophenanthrene (0·1 g.), m. p. 150—151°, which did not depress the m. p. of the specimen prepared above. The infrared spectra of the two specimens were identical.

Reactions of 1,2,4-*Trimethoxybenzene with Phenanthrene*-9,10-*quinone and with Acenaphthenequinone*.—A mixture of 1,2,4-trimethoxybenzene (1·68 g.), phenanthrene-9,10-quinone (1·04 g.), and polyphosphoric acid (10 g.) was heated at 60° for 20 min., poured into ice–water, and extracted with benzene. The extract was washed with aqueous sodium hydrogen carbonate solution, dried, and evaporated giving 2,2′,4,4′,5,5′-hexamethoxybiphenyl (1·02 g.) as needles (from ethanol), m. p. 180—181° (lit.,[11] 177—179°) (Found: C, 64·4; H, 6·7. Calc. for $C_{18}H_{22}O_6$: C, 64·65; H, 6·65%), $\lambda_{max.}$ 2980 Å (log ε 4·009), $\lambda_{infl.}$ 2450 Å (log ε 4·005). The m. p. was not depressed on admixture with an authentic specimen, m. p. 179—181°, prepared by the oxidation of 1,2,4-trimethoxybenzene with chromium trioxide,[11] and the infrared spectra of the two samples were identical. The same product was obtained when acenaphthenequinone was used. No reaction occurred between 1,2,4-trimethoxybenzene and polyphosphoric acid in the absence of the quinones.

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[11] H. G. H. Erdtman, *Proc. Roy. Soc.*, 1933, *A*, **143**, 191.