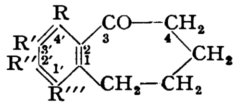
291. *Purpurogallin. Part V. Some Improvements in Synthetical Methods.*

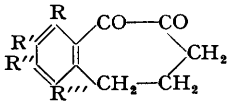
By David Caunt, Wilfrid D. Crow, and Robert D. Haworth.

Improved methods for the conversion of benzo*cyclo*hepten-3-ones of type (I) into benzotropolones of type (III) have been sought. It has been found advantageous to condense compounds of type (I) with ethyl formate and to prepare diones of type (II) by ozonisation of the resulting hydroxymethylene derivatives (V) or their methyl ethers; the dehydrogenation of the diones (II) to benzotropolones of type (III) has been examined under a variety of conditions. As a result of these experiments the yields obtained in the preparation of 4-hydroxy-2′ : 3′-dimethoxybenzo*cyclo*heptatrien-3-one (III; R = R‴ = H, R′ = R″ = OMe) and purpurogallin dimethyl ether (III; R = R′ = R″ = OMe, R‴ = H) have been increased approximately fivefold, and the new methods have also been applied to the synthesis of 4-hydroxy-1′ : 2′ : 3′-trimethoxybenzo*cyclo*heptatrien-3-one (III; R = H, R′ = R″ = R‴ = OMe).

Similar improvements are also realised by the new methods of Barltrop, Johnson, and Meakins (*J.*, 1951, 181).

In Part III (*J.*, 1950, 1631) 4-hydroxy-2′ : 3′-dimethoxybenzo*cyclo*heptatrien-3-one (III; R = R‴ = H, R′ = R″ = OMe) and purpurogallin 2′ : 3′-dimethyl ether (III; R = OH, R′ = R″ = OMe, R‴ = H) * were synthesised by oxidation of 2′ : 3′-dimethoxy- (I; R = R‴ = H, R′ = R″ = OMe) and 2′ : 3′ : 4′-trimethoxy-benzo*cyclo*hepten-3-one (I; R = R′ = R″ = OMe, R‴ = H) respectively with selenium dioxide to the corresponding 3 : 4-diones (II), followed by dehydrogenation with palladium–charcoal. The yields in these two stages were approximately 50% and 8% respectively. New and improved methods described in this communication have improved the overall yields of these two benzotropolones (III; R = R‴ = H, R′ = R″ = OMe) and (III; R = OH, R′ = R″ = OMe, R‴ = H) from 4% to nearly 20%. In addition to this the methods have been successfully applied to the synthesis of 4-hydroxy-1′ : 2′ : 3′-trimethoxybenzo*cyclo*heptatrien-3-one (III; R = H, R′ = R″ = R‴ = OMe), an isomer of purpurogallin trimethyl ether.


(I.)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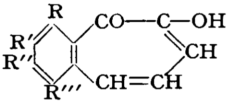
(III.)

The earlier methods described in Part III (*loc. cit.*) suffered from one obvious defect in that the 3 : 4-diones (II) so obtained were difficult to purify from traces of selenium, and it seemed probable that these would poison the catalyst used for the subsequent dehydrogenation, as indeed proved to be the case. Some improvement in purity was effected by shaking an ethereal solution of the dione with aqueous sodium hydrogen sulphide; this removed the selenium but, as small amounts of dione were also removed and traces of sulphur were introduced, other methods of synthesis were sought which avoided the use of selenium dioxide completely.

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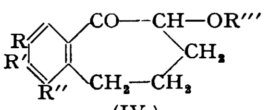
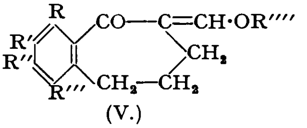
* In this and the following papers, as in previous Parts of the series, formulation of purpurogallin derivatives as (III) does not exclude their existence in the form in which the keto- and hydroxy-groups of the *cyclo*heptatriene ring are interchanged.

It was shown that 1′ : 2′ : 3′-trimethoxybenzo*cyclo*hepten-3-one (I; R = H, R′ = R″ = R‴ = OMe), prepared by an improved method described on p. 1316, was converted into 4-acetoxy-1′ : 2′ : 3′-trimethoxybenzo*cyclo*hepten-3-one (IV; R = R′ = R″ = OMe, R‴ = Ac) by oxidation with lead tetra-acetate in warm acetic acid solution. This acetoxy-compound was hydrolysed by potassium carbonate solution to an oily ketol (IV; R = R′ = R″ = OMe, R‴ = H), but attempted dehydrogenation of the acetoxy-compound or the ketol gave unsatisfactory results. The ketol (IV; R = R′ = OMe, R″ = R‴ = H) prepared similarly from 2′ : 3′-dimethoxybenzo*cyclo*hepten-3-one (I; R = R‴ = H, R′ = R″ = OMe) was an oil, giving a *p*-nitrobenzoate, m. p. 183°, identical with that obtained previously (Part III, *loc. cit.*) by the action of nitrous acid on 4-amino-2′ : 3′-dimethoxybenzo*cyclo*hepten-3-one. The crude ketol (IV; R = R′ = OMe, R″ = R‴ = H) was dehydrogenated with palladium–charcoal in boiling trichlorobenzene to 4-hydroxy-2′ : 3′-dimethoxybenzo*cyclo*heptatrien-3-one (III; R = R‴ = H, R′ = R″ = OMe), m. p. 147° (Part III, *loc. cit.*), but in view of the minute yield (0·5%) this approach was abandoned. Preliminary attempts to convert the ketol (IV; R = R′ = R″ = OMe, R‴ = H) into the corresponding 3 : 4-dione (II; R = H, R′ = R″ = R‴ = OMe) by Oppenauer oxidation (*cyclo*hexanone, aluminium *iso*propoxide) were also discouraging.


(IV.)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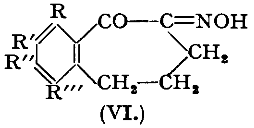
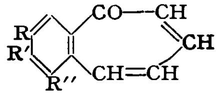

(VI.)

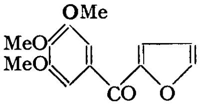
It was shown in Part III (*loc. cit.*) that 4-hydroxymethylene-2′ : 3′-dimethoxybenzo*cyclo*hepten-3-one (V; R = R‴ = R⁗ = H, R′ = R″ = OMe) was readily obtained by condensation of the requisite ketone (I; R = R‴ = H, R′ = R″ = OMe) with ethyl formate under the influence of sodium methoxide. Repetition of this experiment has shown that high yields (85—90%) are readily obtainable, and equally good results have been obtained for the conversion of 1′ : 2′ : 3′- (I; R = H, R′ = R″ = R‴ = OMe) and 2′ : 3′ : 4′-trimethoxybenzo*cyclo*hepten-3-one (I; R = R′ = R″ = OMe, R‴ = H) into the corresponding 4-hydroxymethylene compounds. Treatment with ethereal diazomethane or methanolic hydrogen chloride converted the 4-hydroxymethylene derivatives quantitatively into the corresponding methyl ethers (V; R⁗ = Me); the 2′ : 3′-dimethoxy- and the 1′ : 2′ : 3′-trimethoxy-compound have so far only been obtained as oils. The 4-hydroxymethylene or 4-methoxymethylene derivatives were ozonised in ethyl acetate at −70°, giving 2′ : 3′-dimethoxy-, 1′ : 2′ : 3′-trimethoxy-, and 2′ : 3′ : 4′-trimethoxy-benzo*cyclo*heptene-3 : 4-diones (II) in 100, 87, and 90% yields respectively; the diones were identified by 2 : 4-dinitrophenylhydrazones. Use of excess of ozone resulted in ring fission, and the corresponding γ-*o*-carboxyphenylbutyric acid was isolated in each case.

An alternative approach to the 3 : 4-diones (II) *via* the 4-oximino-derivatives (VI) was investigated previously (Part III, *loc. cit.*). The 4-oximino-derivative (VI; R = R‴ = H, R′ = R″ = OMe), obtained in 50% yield by the action of *iso*amyl nitrite on the corresponding ketone (I) in the presence of methanolic hydrogen chloride, was hydrolysed with pyruvic acid and strong hydrochloric acid, but gave only a 30% yield of the 3 : 4-dione as an oil, together with much resinous material. Recently Barltrop, Johnson, and Meakins (*J.*, 1951, 181) have modified and improved the preparation of 2′ : 3′-dimethoxy-4-oximinobenzo*cyclo*hepten-3-one (VI; R = R‴ = H, R′ = R″ = OMe), and shown that hydrolysis is effected in high yield by formaldehyde and dilute hydrochloric acid, giving the 3 : 4-dione (II; R = R‴ = H, R′ = R″ = OMe) as a crystalline solid. Clearly our earlier conditions were too drastic, and resulted in further condensation of the dione to resinous material. We have confirmed the results of Barltrop, Johnson, and Meakins and obtained 2′ : 3′-dimethoxybenzo*cyclo*heptene-3 : 4-dione (II; R = R‴ = H, R′ = R″ = OMe), m. p. 104°, in overall yield of 68%. Extension of this method to the trimethoxy-series has resulted in the formation of 1′ : 2′ : 3′- and 2′ : 3′ : 4′-trimethoxybenzo*cyclo*heptene-3 : 4-dione (II) in overall yields of 75%. These diones do not crystallise and have been characterised as their 2 : 4-dinitrophenylhydrazones. In agreement with previous experiments in the dimethoxy-series it was found that 1′ : 2′ : 3′-trimethoxybenz*cyclo*heptene-3 : 4-dione (II; R = H, R′ = R″ = R‴ = OMe) gave only a poor yield (approximately 10%) of 4-hydroxy-1′ : 2′ : 3′-trimethoxybenzo*cyclo*heptatrien-3-one (III; R = H, R′ = R″ = R‴ = OMe) when dehydrogenated with palladium–charcoal in the usual way. This yield was doubled when the dione employed for dehydrogenation was prepared by ozonolysis of the 4-hydroxymethylene derivative or by hydrolysis of the 4-oximino-derivative. Similar results were obtained with the other diones (II; R = R‴ = H, R′ = R″ = OMe) and (II; R = R′ = R″ = OMe, R‴ = H). A quantitative study of this dehydrogenation reaction has shown that the volume of hydrogen evolved bears little relation to the amount of product formed, although the ratio of the two is approximately constant for a given catalyst. The yields could not be increased by replacing trichlorobenzene by other solvents, or by addition of maleic anhydride to the system, and chloranil and *p*-benzoquinone were found to be ineffective as dehydrogenating agents.

The synthesis of purpurogallin 2′ : 3′-dimethyl ether (Part III, *loc. cit.*) was repeated, extreme precautions being taken against demethylation during the isolation process. The failure to obtain the unknown 2′ : 3′ : 4′-trimethyl ether proved conclusively that demethylation was effected during the dehydrogenation. In this connection it is noteworthy that dehydrogenation of 1′ : 2′ : 3′-trimethoxybenzo*cyclo*hepten-3-one (I; R = H, R′ = R″ = R‴ = OMe) gave in low yield a phenol, m. p. 130—131°, analysing as a dimethyl ether of 1′ : 2′ : 3′-trihydroxybenzo*cyclo*heptatrien-3-one (VII; R = R′ = R″ = OH). The demethylation being assumed to have resulted from the usual activation at positions *ortho* and *para* to a *meta*-directing substituent, this phenol would be expected to be 2′-hydroxy-1′ : 3′-dimethoxybenzo*cyclo*heptatrien-3-one (VII; R = R″ = OMe, R′ = OH). The formation of purpurogallin dimethyl ether may be explained on a similar basis.

(VII.)





(VIII.)

During the course of the experiments outlined above it was decided to attempt the synthesis of 4-hydroxy-1′ : 2′ : 3′-trimethoxybenzo*cyclo*heptatrien-3-one (III; R = H, R′ = R″ = R‴ = OMe) by direct rearrangement of 2-furyl 3′ : 4′ : 5′-trimethoxyphenyl ketone (VIII). This compound was prepared by the action of 3 : 4 : 5-trimethoxybenzoyl chloride on furan in nitrobenzene, aluminium chloride being used as catalyst. It was obtained as a nearly colourless solid, m. p. 108—109°, giving a red 2 : 4-dinitrophenylhydrazone, m. p. 201—202°. Rearrangement could not be effected by 20% hydrochloric acid at 150°, the products giving unchanged ketone on remethylation. The use of 46% hydrobromic acid resulted in extensive resinification, and this line of attack was abandoned.

EXPERIMENTAL.

*2′ : 3′-Dimethoxy-4-methoxymethylenebenzo*cyclo*hepten-3-one* (V; R = R‴ = H, R′ = R″ = OMe, R⁗ = Me).—4-Hydroxymethylene-2′ : 3′-dimethoxybenzo*cyclo*hepten-3-one (Part III, *loc. cit.*) (10·0 g.) was refluxed for 30 minutes with methanol (100 c.c.) containing a little hydrogen chloride. Removal of the solvent gave the *methyl ether* (10·4 g.) which separated from methanol in colourless plates, m. p. 117° (Found: C, 68·3; H, 7·1. $C_{15}H_{18}O_4$ requires C, 68·6; H, 6·9%).

*2′ : 3′-Dimethoxybenzo*cyclo*heptene-3 : 4-dione* (II; R = R‴ = H, R′ = R″ = OMe).—The methyl ether, described above (10·0 g.), in ethyl acetate (50 c.c.) was cooled to −70° and allowed to react with one molecular equivalent of ozone. The resultant solution was hydrogenated over palladium–charcoal with cooling until one mol. of hydrogen was absorbed. Filtration and removal of the solvent under reduced pressure yielded the dione (8·9 g.) as a yellow oil. Crystallisation first from water and then from *cyclo*hexane gave yellow prisms, m. p. 104° (Found: C, 66·4; H, 5·9. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%). The *disemicarbazone* crystallised from alcohol in colourless plates, m. p. 245° (Found: C, 50·8; H, 5·5. $C_{15}H_{22}O_5N_6$ requires C, 50·8; H, 5·8%).

When excess of ozone was used a small amount of *γ-(2-carboxy-4 : 5-dimethoxyphenyl)butyric acid* was isolated by extraction with sodium hydrogen carbonate solution and separated from alcohol as colourless prisms, m. p. 165° (Found: C, 58·4; H, 6·2. $C_{13}H_{16}O_6$ requires C, 58·2; H, 6·0%). Dehydrogenation of the 3 : 4-dione in the usual way (Part III, *loc. cit.*) gave 4-hydroxy-2′ : 3′-dimethoxybenzo*cyclo*heptatrien-3-one (III; R = R‴ = H, R′ = R″ = OMe) in 22% yield.

*4-Hydroxy-2′ : 3′-dimethoxybenzo*cyclo*hepten-3-one* (IV; R = R′ = OMe, R″ = R‴ = H).—2′ : 3′-Dimethoxybenzo*cyclo*hepten-3-one (5·0 g.) was heated on the water-bath for 2 hours with lead tetra-acetate (8·0 g.) in dry acetic acid (25 c.c.), and the solution was diluted with water (250 c.c.) and extracted with ether. After being washed (to remove acetic acid), the extracts were concentrated, giving a light yellow oil (5·2 g.) which could not be obtained crystalline. After distillation the oil (b. p. 165—185°/0·01 mm.), which did not solidify, was hydrolysed with aqueous-methanolic potassium carbonate on the water-bath for 2 hours. The product, a dark brown oil (4·5 g.), did not crystallise and decomposed on attempted distillation. On storage unchanged 2′ : 3′-dimethoxybenzo*cyclo*hepten-3-one (2·1 g.) crystallised and the residual ketol gave, in the usual way, a *p*-nitrobenzoate, which separated from *cyclo*hexane in colourless prisms, m. p. 183°, identical with the product obtained from 4-amino-2′ : 3′-dimethoxybenzo*cyclo*hepten-3-one (Part III, *loc. cit.*).

The ketol (3·0 g.; crude) was dehydrogenated in the usual way giving 4-hydroxy-2′ : 3′-dimethoxybenzo*cyclo*heptatrien-3-one (0·016 g.) which crystallised from *cyclo*hexane in deep yellow prisms, m. p. 145—146°.

*1′ : 2′ : 3′-Trimethoxybenzo*cyclo*hepten-3-one* (I; R = H, R′ = R″ = R‴ = OMe).—δ-(2 : 3 : 4-Trimethoxyphenyl)valeric acid (13·4 g.) (Part I, *J.*, 1948, 1051) in dry benzene (150 c.c.) was treated for 2 hours at 0° with phosphorus pentachloride (11·0 g.) and pyridine (0·1 c.c.), and the reaction completed by warming on the water-bath for 10 minutes. The solution was again cooled to 0°, added to an ice-cold solution of stannic chloride (redistilled; 8·5 c.c.) in dry benzene (2 l.), kept for 15 hours at 0°, and hydrolysed by addition of ice (250 g.) and concentrated hydrochloric acid (250 c.c.). The benzene layer was washed successively with water, 20% sodium hydroxide solution (500 c.c.), and water, dried, and freed from solvent. Distillation of the oily residue gave the ketone (8·8 g.) as a colourless oil, b. p. 152—155°/0·3 mm.* Acidification of the alkaline extracts afforded a little unchanged acid (3·0 g.). The ketone gave a 2 : 4-*dinitrophenylhydrazone*, existing in two interchangeable forms: red prisms (from acetic acid), m. p. 181—182° (Part I, *loc. cit.*), and yellow needles (from alcohol), m. p. 181—182° (Found: C, 56·0; H, 5·2; N, 12·9. $C_{20}H_{22}O_7N_4$ requires C, 55·8; H, 5·1; N, 13·0%), and a *semicarbazone*, which crystallised from aqueous methanol in colourless needles, m. p. 197—198° (Found: C, 58·5; H, 6·9; N, 13·9. $C_{15}H_{21}O_4N_3$ requires C, 58·6; H, 6·9; N, 13·7%).

*Dehydrogenation of 1′ : 2′ : 3′-Trimethoxybenzo*cyclo*hepten-3-one* (I; R = H, R′ = R″ = R‴ = OMe).—The ketone described above (5·0 g.) was refluxed for 15 hours with 10% palladium–charcoal (5·0 g.) in 1 : 2 : 4-trichlorobenzene (20 c.c.) with a current of nitrogen. After dilution with ether (10 volumes) and filtration the solution was washed with sodium hydrogen carbonate solution (which removed traces of tarry and acidic material), then repeatedly with sodium hydroxide. Acidification of the sodium hydroxide extracts afforded a small quantity (0·06 g.) of a colourless *phenol* (possibly VII; R′ = R″ = OMe, R′ = H), which separated from light petroleum (b. p. 40—60°) in needles, m. p. 130—131° (Found: C, 65·4; H, 6·7; OMe, 26·2. $C_{13}H_{12}O_4$ requires C, 65·5; H, 7·0; OMe, 26·8%), which gave a slow positive test with Brady's reagent.

The neutral residues of the dehydrogenation were treated with Girard reagent T in the usual way, but only unchanged 1′ : 2′ : 3′-trimethoxybenzo*cyclo*hepten-3-one (2·0 g.) was recovered.

*4-Hydroxymethylene-1′ : 2′ : 3′-trimethoxybenzo*cyclo*hepten-3-one* (V; R = R⁗ = H, R′ = R″ = R‴ = OMe) was prepared in 85% yield from 1′ : 2′ : 3′-trimethoxybenzo*cyclo*hepten-3-one (I; R = H, R′ = R″ = R‴ = OMe) by the method described in Part III (*loc. cit.*). It crystallised from aqueous methanol in colourless needles, m. p. 71·5—72·5° (Found: C, 64·5; H, 6·3. $C_{15}H_{18}O_3$ requires C, 64·7; H, 6·5%), and gave a violet-red ferric colour. The 2 : 4-*dinitrophenylhydrazone* crystallised in dark red plates (from acetic acid), m. p. 176—177° (Found: C, 54·6; H, 4·7; N, 12·5. $C_{21}H_{22}O_8N_4$ requires C, 55·0; H, 4·8; N, 12·2%).

Methylation of the hydroxymethylene compound (2·0 g.) with excess of ethereal diazomethane gave the *methyl ether* (2·0 g.) which gave no ferric colour and crystallised from aqueous methanol in colourless needles, m. p. 107—108° (Found: C, 66·0; H, 6·7. $C_{16}H_{20}O_5$ requires C, 65·7; H, 6·9%).

*1′ : 2′ : 3′-Trimethoxy-4-oximinobenzo*cyclo*hepten-3-one* (VI; R = H; R′ = R″ = R‴ = OMe) was prepared in 85% yield as described by Barltrop, Johnson, and Meakins (*loc. cit.*) by the action of *iso*amyl nitrite in ethereal hydrogen chloride on the ketone (I; R = H, R′ = R″ = R‴ = OMe) at −70°. The hydrochloride of the product was precipitated by the addition of light petroleum (b. p. 40—60°). The resultant oil was converted into the base with sodium hydrogen carbonate solution, and crystallised from aqueous methanol in pale yellow hydrated prisms, m. p. 132—133° (Found: C, 56·4; H, 6·4; N, 4·8. $C_{14}H_{17}O_5N,H_2O$ requires C, 56·6; H, 6·4; N, 4·7%), or from benzene–light petroleum (b. p. 40—60°) in pale yellow needles, m. p. 135—136° (Found: C, 60·1; H, 6·1. $C_{14}H_{17}O_5N$ requires C, 60·1; H, 6·1%).

*1′ : 2′ : 3′-Trimethoxybenzo*cyclo*heptene-3 : 4-dione* (II; R = H, R′ = R″ = R‴ = OMe).—(*a*) The ketone (I; R = H, R′ = R″ = R‴ = OMe) (10·0 g.) was refluxed for 4 hours in *n*-butyl alcohol (75 c.c.) with selenium dioxide (4·44 g.), diluted with ether (2 volumes), and filtered, and all solvents were then removed under reduced pressure. Distillation of the residual oil gave a yellow oil (8·1 g.), b. p. 140—170°/0·2 mm., which was dissolved in ether, and passed through a column of alumina (5 × 0·5 cm.). Continued elution with ether (total, 500 c.c.) gave, after concentration, an oil, which on distillation yielded unchanged ketone (I; R = H, R′ = R″ = R‴ = OMe) (0·65 g.) and the 3 : 4-dione as a viscous yellow oil (7·0 g.), b. p. 166—170°/0·2 mm., which could not be obtained crystalline. The dione dissolved in aqueous sodium hydroxide to give a yellow solution, and gave a 2 : 4-*dinitrophenylhydrazone*, crystallising from acetic acid in orange needles, m. p. 177—178° (Found: C, 54·3; H, 4·6; N, 12·5. $C_{20}H_{20}O_8N_4$ requires C, 54·1; H, 4·5; N, 12·6%).

(*b*) 4-Hydroxymethylene-1′ : 2′ : 3′-trimethoxybenzo*cyclo*hepten-3-one (3·0 g.) was submitted to ozonolysis as described for the methyl ether of the 2′ : 3′-dimethoxy-analogue (p. 1315). Extraction of the dione solution with sodium hydrogen carbonate solution gave a little γ-(6-carboxy-2 : 3 : 4-trimethoxyphenyl)butyric acid, m. p. 140—141° [in Part I (*loc. cit.*) this was reported as m. p. 132°], identical with an authentic specimen. Evaporation of the organic layer yielded the 3 : 4-dione (2·35 g.) as a yellow oil, b. p. 166—170°/0·2 mm.

(*c*) The 3 : 4-dione was also prepared in 94% yield by hydrolysis of 1′ : 2′ : 3′-trimethoxy-4-oximinobenzo*cyclo*hepten-3-one as described for the 2′ : 3′-dimethoxy-analogue.

*4-Acetoxy-1′ : 2′ : 3′-trimethoxybenzo*cyclo*hepten-3-one* (IV; R = R′ = R″ = OMe, R‴ = Ac) prepared in 80% yield as described for the dimethoxy-analogue (p. 1315) was obtained as colourless needles

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* The b. p. of this compound was erroneously recorded in Part I as 170°/0·3 mm.

(from *cyclo*hexane), m. p. 97—98° (Found : C, 62·2; H, 6·5. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·5%). Hydrolysis by the method described previously gave a yellow oily ketol which could not be satisfactorily distilled and did not crystallise. This compound (2·0 g.) was refluxed for 6 hours with *cyclo*hexanone (10 c.c.), toluene (100 c.c.), and aluminium *iso*propoxide (1·4 g.), and the mixture hydrolysed with hydrochloric acid (250 c.c.; 10%). Evaporation of the organic layer gave a deep red oil (1·75 g.) which on distillation gave a viscous orange oil (1·2 g.), b. p. 195—210°/0·1 mm. Treatment with Brady's reagent in large excess gave a small amount (0·8 g.) of a product, crystallising from acetic acid in orange plates, m. p. 257—259° (Found : C, 50·3; H, 4·2; N, 17·8. $C_{26}H_{24}O_{11}N_8$ requires C, 50·0; H, 3·9; N, 17·9%). The same product, probably the *bis*-2 : 4-*dinitrophenylhydrazone* of the dione, was also obtained by prolonged action of Brady's reagent on 1′ : 2′ : 3′-trimethoxy-4-oximinobenzo*cyclo*hepten-3-one. Dehydrogenation of the ketol acetate in the usual way gave a small amount of unidentified phenol crystallising from *cyclo*hexane in colourless needles, m. p. 152—153° (Found : C, 63·4; H, 5·6%).

4-*Hydroxy*-1′ : 2′ : 3′-*trimethoxybenzo*cyclo*heptatrien*-3-*one* (III; R = H, R′ = R″ = R‴ = OMe).—1′ : 2′ : 3′-Trimethoxybenzo*cyclo*heptene-3 : 4-dione [0·5 g.; obtained by method (*b*) above] was refluxed for 10 hours with 10% palladium–charcoal (0·5 g.) (*Org. Synth.*, **26**, 78) in 1 : 2 : 4-trichlorobenzene (5 c.c.) in a current of carbon dioxide. The hydrogen evolved was measured over 40% potassium hydroxide solution. The mixture was diluted with ether and filtered, and the catalyst extracted twice with boiling 10% sodium hydroxide solution. The product recovered by acidification was taken up in ether and mixed with the original organic solvents.

The organic solvents were extracted with sodium hydrogen carbonate solution, then twice with 10% sodium hydroxide solution, and finally washed with water. Acidification of the bicarbonate extract gave an acid (*ca.* 0·04 g.) which was not further investigated. Similar treatment of the combined sodium hydroxide extracts and washings gave, after isolation with ether and crystallisation from *cyclo*hexane, 4-*hydroxy*-1′ : 2′ : 3′-*trimethoxybenzo*cyclo*heptatrien*-3-*one* (0·105 g.) which separated in yellow needles, m. p. 91—92° (Found : C, 63·7; H, 5·2. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·4%). This was soluble in alkali to give a yellow solution, gave a crimson ferric colour, extractable by chloroform, and a crimson coupling product with diazotised *p*-toluidine.

The ultra-violet spectrum was measured in M/20,000 solution in methanol. The values obtained for $\lambda_{max.}$, in mμ., are followed in parentheses by the corresponding values for $\log_{10} \varepsilon$: 208 (4·20), 280 (4·49), 297·5 (4·25), 350 (3·81), 405 (3·74). Points of inflexion were observed at 273 (4·43) and 450 (2·68).

4-*Hydroxymethylene*-2′ : 3′ : 4′-*trimethoxybenzo*cyclo*hepten*-3-*one* (V; R = R′ = R″ = OMe, R‴ = R⁗ = H), prepared from 2′ : 3′ : 4′-trimethoxybenzo*cyclo*hepten-3-one (Part III, *loc. cit.*) in 88% yield by the method described previously (p. 1316), crystallised in colourless needles from aqueous methanol, m. p. 112—113° (Found : C, 65·6; H, 6·4. $C_{15}H_{18}O_5$ requires C, 64·7; H, 6·5%), and gave a violet-red ferric colour. The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in dark red needles, m. p. 204—205° (Found : C, 54·9; H, 4·6; N, 12·0. $C_{21}H_{22}O_8N_4$ requires C, 55·0; H, 4·8; N, 12·2%).

Attempted methylation of the hydroxymethylene compound with sodium methoxide and methyl iodide resulted in the formation of 2′ : 3′ : 4′-*trimethoxy*-4-*methylbenzo*cyclo*hepten*-3-*one* which separated from aqueous methanol in needles, m. p. 87—88° (Found : C, 68·2; H, 7·4. $C_{15}H_{20}O_4$ requires C, 68·2; H, 7·6%). The use of excess of ethereal diazomethane gave 2′ : 3′ : 4′-*trimethoxy*-4-*methoxymethylenebenzo*cyclo*hepten*-3-*one* (V; R = R′ = R″ = OMe, R‴ = H, R⁗ = Me) in 95% yield as a colourless oil, b. p. 158—160°/0·1 mm., which could not be obtained crystalline. It gave no ferric colour, but formed a 2 : 4-*dinitrophenylhydrazone*, separating from aqueous acetic acid in dark red needles, m. p. 189—190° (Found : C, 56·1; H, 5·2; N, 11·8. $C_{22}H_{24}O_8N_4$ requires C, 55·9; H, 5·1; N, 11·9%).

2′ : 3′ : 4′-*Trimethoxy*-4-*oximinobenzo*cyclo*hepten*-3-*one* (IV; R = R′ = R″ = OMe, R‴ = H), prepared as described for the 1′ : 2′ : 3′-trimethoxy-isomer (p. 1316) (yield 85%), crystallised from benzene–ligroin in pale yellow prisms, m. p. 175—176° (Found : C, 60·0; H, 6·2; N, 5·0. $C_{14}H_{17}O_5N$ requires C, 60·1; H, 6·1; N, 5·0%).

2′ : 3′ : 4′-*Trimethoxybenzo*cyclo*heptene*-3 : 4-*dione* (II; R = R′ = R″ = OMe; R‴ = H).—(i) 4-Hydroxymethylene-2′ : 3′ : 4′-trimethoxybenzo*cyclo*hepten-3-one (2·0 g.) was ozonised as described for the 1′ : 2′ : 3′-trimethoxy-isomer (p. 1316). There was obtained a little γ-(2-carboxy-3 : 4 : 5-trimethoxyphenyl)butyric acid, m. p. 146—147°, identical with an authentic specimen, together with the 3 : 4-dione (1·62 g.) obtained as a yellow oil and identified as its 2 : 4-dinitrophenylhydrazone, m. p. 180—181°.

(ii) The 3 : 4-dione was obtained in 90% yield as a yellow oil by hydrolysis of 2′ : 3′ : 4′-trimethoxy-4-oximinobenzo*cyclo*hepten-3-one as described for the 2′ : 3′-dimethoxy-isomer, and identified as its 2 : 4-dinitrophenylhydrazone.

Dehydrogenation of 2′ : 3′ : 4′-*Trimethoxybenzo*cyclo*heptene*-3 : 4-*dione*.—The 3 : 4-dione obtained above by ozonolysis was dehydrogenated as described for the 1′ : 2′ : 3′-trimethoxy-isomer, and the alkaline extracts neutralised carefully at −10° to avoid demethylation. The solution was extracted with ether, then washed repeatedly with water, and the ether removed. Crystallisation of the residue from methanol gave, in 20% yield, orange plates, m. p. 156—157°, identical with an authentic specimen of purpurogallin dimethyl ether.

2-*Furyl* 3′ : 4′ : 5′-*Trimethoxyphenyl Ketone*.—3 : 4 : 5-Trimethoxybenzoyl chloride (11·5 g.) and furan (3·4 g.) in dry nitrobenzene (50 c.c.) were added gradually, with shaking, to a solution of anhydrous aluminium chloride (8·0 g.) in dry nitrobenzene (50 c.c.) at 0°. After 24 hours at room temperature the mixture was decomposed with ice (100 g.) and hydrochloric acid (10N.; 100 c.c.), and the nitrobenzene removed by steam-distillation. The residue was treated with methyl sulphate and sodium hydroxide solution, and the neutral fraction extracted with chloroform. The residue after evaporation of the chloroform was repeatedly extracted with boiling *cyclo*hexane, and the combined extracts were evaporated to dryness. Recrystallisation of the product from a little ether gave the *ketone* (6·65 g.) as pale cream-coloured needles, m. p. 108—109° (Found : C, 64·2; H, 5·3. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·4%). The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in fine red needles, m. p. 201—202° (Found : C, 54·2; H, 3·7; N, 13·1. $C_{20}H_{18}O_8N_4$ requires C, 54·3; H, 4·1; N, 12·7%).

On treatment of the ketone with hydrochloric acid (5N.) at 150° for 4 hours a pale yellow amorphous product was obtained. Methylation of this gave the original ketone, m. p. 108—109°. Treatment of the ketone with hydrobromic acid (46%) under reflux for 30 minutes gave a tarry red mass from which no tractable products could be isolated.

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