

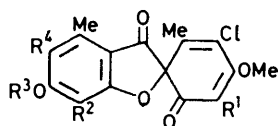
Depsidone Synthesis. Part 17.¹ The Photochemistry of Grisa-3',5'-diene-2',3-diones

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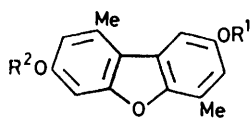
The photoconversion of spiro[benzofuran-2,1'-cyclohexa-3',5'-diene]-2',3(2*H*)-diones (grisa-3',5'-diene-2',3-diones) to dibenzofurans is described, and a mechanism for this reaction is proposed.

In the preceding paper¹ we reported the thermal and acid- and base-catalysed rearrangement of linearly conjugated grisadienediones to depsidones. In view of the extensive investigations on the photochemistry of linearly conjugated cyclohexadienones² it was of interest to examine that of the grisadienediones.

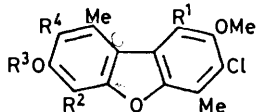
The first compound studied was the grisadienedione (1)



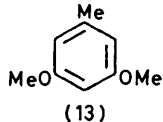
- (1) $R^1 = R^4 = \text{Cl}, R^2 = R^3 = \text{H}$
 (2) $R^1 = R^4 = \text{Cl}, R^2 = \text{H}, R^3 = \text{Me}$
 (3) $R^1 = \text{Me}, R^2 = R^3 = R^4 = \text{H}$
 (4) $R^1 = R^2 = \text{Me}, R^3 = R^4 = \text{H}$



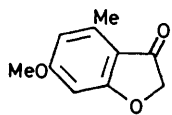
- (5) $R^1 = R^2 = \text{Me}$
 (6) $R^1 = \text{H}, R^2 = \text{Me}$
 (7) $R^1 = \text{Me}, R^2 = \text{H}$



- (8) $R^1 = R^4 = \text{Cl}, R^2 = R^3 = \text{H}$
 (9) $R^1 = R^4 = \text{Cl}, R^2 = \text{H}, R^3 = \text{Me}$
 (10) $R^1 = R^4 = \text{Cl}, R^2 = \text{H}, R^3 = \text{CH}_2\text{Ph}$
 (11) $R^1 = \text{Me}, R^2 = R^3 = R^4 = \text{H}$
 (12) $R^1 = R^2 = \text{Me}, R^3 = R^4 = \text{H}$



(13)

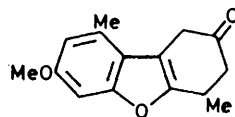


(14)

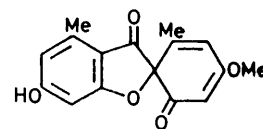
which was irradiated in benzene through borosilicate glass with light centred at 350 nm in order to excite the dienone chromophore. Only one product was isolated and that in good yield. This photoproduct had lost the elements of carbon dioxide and did not exhibit a carbonyl band in its i.r. spectrum. The n.m.r. spectrum exhibited signals due to a methoxy-group, two aromatic methyl groups, and an aromatic proton. The compound was phenolic and the electronic spectrum of the derived methyl ether was suggestive of a dibenzofuran.³ The benzyl ether of the photoproduct was prepared. On saturation of the signal due to the benzylic protons in the n.m.r. spectrum of this ether there was a 39% nuclear Overhauser effect at the aromatic proton. Hence the aromatic proton and the phenolic hydroxy-group must still be in an *ortho*-arrangement in the photoproduct. The methyl ether of the photoproduct was subjected to hydrogenolytic dechlorination and thus yielded the di-*O*-methyl ether of a dimethyldibenzofurandiols tentatively

formulated as (5) on the grounds of its ¹H n.m.r. spectrum. The photoproduct, its methyl ether, and its benzyl ether were therefore formulated as (8), (9), and (10).

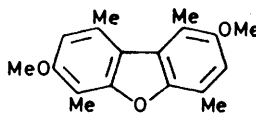
The structure of the dibenzofuran (5) was proved by rational synthesis. Friedel-Crafts acylation of di-*O*-methylorcinol (13) with chloroacetyl chloride and aluminium chloride as catalyst gave directly the β-coumaranone (14). This was allowed to react with (*E*)-pent-3-en-2-one in presence of sodium methoxide. Michael addition and subsequent aldol condensation occurred and the dihydrobenzofuranone (15) resulted. This compound was dehydrogenated with palladium-charcoal in boiling diphenyl ether which furnished the dibenzofuranol (6). This on methylation gave the degradation product (5).



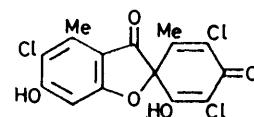
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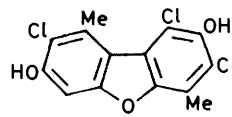
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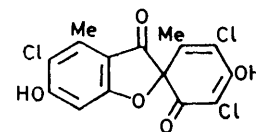
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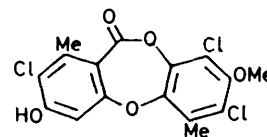
(18)



(19)



(20)

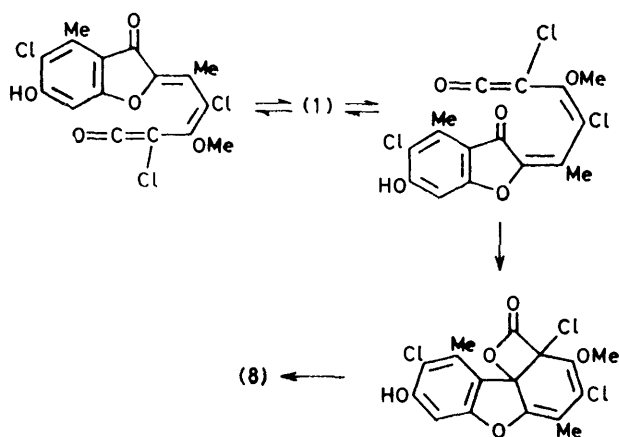


(21)

The grisadienediones (2)—(4) and (16) on irradiation gave the dibenzofurans (9), (11), (12), and (7). The structure of the dibenzofuranol (7) was confirmed since it was different to the dibenzofuranol (6) yet on methylation they both yielded the same methyl ether (5). The structure of the dibenzofuranol (12) was also con-

firmed by its conversion by methylation and hydrolytic dechlorination into the known dibenzofuran (17).⁴ The photoconversion of the grisadienedione (18) into the dibenzofuranol (19) is slower than the others presumably because phototautomerism to the dienone (20) is necessary.

The depsidone (21) cannot be an intermediate in the formation of the dibenzofuran (8) since it was unchanged under the reaction conditions. Hence we propose that excitation of the dienone chromophore of the grisadienedione causes either concerted or radical ring-opening to pairs of stereoisomeric dienylketens. Only one member of each pair is able, because of its stereochemistry, to undergo a thermal intramolecular $\pi_a + \pi_s$ cyclization yielding a β -lactone. Loss of carbon dioxide would then yield the products. This mechanism is illustrated for the conversion (1) \rightarrow (8) (Scheme). Linearly



SCHEME

conjugated cyclohexadienediones are known to yield dienylketens on u.v. irradiation,² and cyclizations of ketens^{5,6} similar to the above, which yield thermally unstable β -lactones,⁷ are also known.

Irradiation of the grisadienedione (2) in methanol did not result in the trapping of the dienylketen. Presumably intramolecular cyclization is more rapid than nucleophilic attack by methanol. A similar case has been reported for the photochemistry of umbellulone where the dienylketen could be observed spectroscopically at low temperature but was not trapped by methanol at room temperature.⁸

EXPERIMENTAL

General directions have been given previously.⁹ Electronic spectra were determined for ethanolic solutions using a Beckman Acta MIV spectrophotometer.

General Method for Photolysis of Grisadienediones.—The grisadienedione in dry benzene solution contained in a borosilicate glass Schlenk tube and maintained under dry nitrogen was irradiated with an apparatus containing sixteen vertically mounted 3500 Å lamps arranged in a circle. The solution was kept at *ca.* 35 °C by air cooling with an electric fan mounted below the photolysis tube. After irradiation for the stated time the solvent was removed

under reduced pressure and the residue was purified by preparative t.l.c. (ethyl acetate–light petroleum).

Photolysis of 3',5,5'-Trichloro-6-hydroxy-4'-methoxy-4,6'-dimethylspiro[benzofuran-2,1'-cyclohexa-3',5'-diene]-2',3(2H)-dione (1).—The grisadienedione (1) (50 mg) was irradiated in benzene (150 ml) for 0.75 h. This gave 2,7,9-trichloro-8-methoxy-1,6-dimethyldibenzofuran-3-ol (8) (25.8 mg) as needles (from dichloromethane–light petroleum), m.p. 184–186 °C (Found: M^+ , 343.9773. $^{12}\text{C}_{15}^{1}\text{H}_{11}^{35}\text{Cl}_3^{16}\text{O}_3$ requires M , 343.9774); $\delta(\text{CDCl}_3, 90 \text{ MHz})$ 2.54 (3 H, s, Me), 3.09 (3 H, s, $W_{1/2}$ 1.8 Hz, Me), 3.91 (3 H, s, OMe), and 7.02 (1 H, s, $W_{1/2}$ 2.1 Hz, ArH). Methylation in the usual way with iodomethane and potassium carbonate in dry *NN*-dimethylformamide under dry nitrogen gave 1,3,8-trichloro-2,7-dimethoxy-4,9-dimethyldibenzofuran (9) as needles (from chloroform–methanol), m.p. 179–180 °C (Found: C, 53.5; H, 3.7; Cl, 29.6%; M^+ , 358, 360, 362. $\text{C}_{16}\text{H}_{13}\text{Cl}_3\text{O}_3$ requires C, 53.4; H, 3.65; Cl, 29.6%; M , 358, 360, 362); $\delta(\text{CDCl}_3, 90 \text{ MHz})$ 2.52 (3 H, s, Me), 3.06 (3 H, s, $W_{1/2}$ 1.7 Hz, Me), 3.91 and 3.95 (each 3 H, s, OMe), and 6.90 (1 H, s, $W_{1/2}$ 1.7 Hz, ArH); λ_{max} 237, 260, 269.5, 305, and 314 nm (ϵ 29 300, 9 900, 13 000, 19 200, and 18 700). Benzylation in the usual way with benzyl bromide and potassium carbonate in *NN*-dimethylformamide under dry nitrogen gave 7-benzyloxy-1,3,8-trichloro-2-methoxy-4,9-dimethyldibenzofuran (10) as needles (from chloroform–methanol), m.p. 161–163 °C (Found: C, 60.55; H, 4.0; Cl, 24.65. $\text{C}_{22}\text{H}_{17}\text{Cl}_3\text{O}_3$ requires C, 60.65; H, 3.95; Cl, 24.4%); $\delta(\text{CDCl}_3, 90 \text{ MHz})$ 2.49 (3 H, s, Me), 3.04 (3 H, s, $W_{1/2}$ 1.3 Hz, Me), 3.89 (3 H, s, OMe), 5.17 (2 H, s, CH_2), 6.89 (1 H, s, $W_{1/2}$ 1.9 Hz, ArH), and 7.27–7.58 (5 H, m, Ph).

Hydrogenolysis of 1,3,8-Trichloro-2,7-dimethoxy-4,9-dimethyldibenzofuran (9).—The dibenzofuran (9) (20 mg) in methanol (30 ml), ethyl acetate (10 ml), and triethylamine (0.5 ml) was shaken under 4 atm of hydrogen with 10% palladium-charcoal (Engelhard) (100 mg) for 26 h. The usual work-up gave 3,8-dimethoxy-1,6-dimethyldibenzofuran (5) (12 mg) as prisms (from methanol), m.p. 119–120 °C (Found: M^+ , 256.1076. $^{12}\text{C}_{16}^1\text{H}_{16}^{16}\text{O}_3$ requires M , 256.1099); $\delta(\text{CDCl}_3, 90 \text{ MHz})$ 2.53 (3 H, m, $W_{1/2}$ 1.3 Hz, 6-Me), 2.70 (3 H, m, $W_{1/2}$ 1.8 Hz, 1-Me), 3.86 and 3.87 (each 3 H, s, OMe), 6.75 and 6.98 (2 H, br AB, $J_{2,4}$ 2.0 Hz, 2- and 4-H), and 6.85 and 7.28 (2 H, br AB, $J_{7,9}$ 2.5 Hz, 7- and 9-H); irradiation at δ 2.53 sharpened the AB system due to H-7,9 and irradiation at δ 2.70 sharpened the AB system due to H-2,4; λ_{max} 211, 227, 262, 295, 298, 304, and 317 nm (ϵ 24 200, 29 600, 16 400, 16 900, 16 600, 16 300, and 7 200).

6-Methoxy-4-methylbenzofuran-3(2H)-one (14).—This coumaranone (14) was prepared by the method of Brewer and Elix.¹⁰ The crude product was steam distilled and then crystallized from dichloromethane–light petroleum to give pale-yellow prisms, m.p. 118–119 °C (lit.,¹⁰ m.p. 105 °C) (Found: C, 67.2; H, 5.35%; M^+ , 178. Calc. for $\text{C}_{10}\text{H}_{10}\text{O}_3$; C, 67.4; H, 5.65%; M , 178); $\delta(\text{CCl}_4, 60 \text{ MHz})$ 2.45 (3 H, s, Me), 3.73 (3 H, s, OMe), 4.37 (2 H, s, CH_2), and 6.18 (2 H, apparent s, ArH).

1,4-Dihydro-7-methoxy-4,9-dimethyldibenzofuran-2(3H)-one (15).—This method is based on that of MacMillan *et al.*¹¹ The coumaranone (14) (4.0 g), (*E*)-pent-3-en-2-one (1.9 g), methanolic sodium methoxide (2m; 1.9 ml), and dry dioxan (100 ml) were mixed together and set aside for 21 h. Acetic acid (10 ml) was added and the solution was evaporated under reduced pressure. The residue, in ethyl acetate, was then washed in turn with water, saturated

aqueous sodium hydrogencarbonate, water, and finally saturated brine. The crude product was chromatographed over silica gel with 2.5–5% ethyl acetate–light petroleum as eluant. Early fractions gave the *dibenzofuranone* (15) (1.0 g) as rods (from dichloromethane–light petroleum), m.p. 115–116 °C (Found: C, 73.85; H, 6.8%; M^+ , 244. $C_{15}H_{16}O_3$ requires C, 73.75; H, 6.6%; M , 244); $\delta(CDCl_3, 90\text{ MHz})$ 1.36 (3 H, d, $J_{4,Me}$ 7.0 Hz, 4-Me), 2.44 (3 H, s, $W_{1,3}$ 2.1 Hz, 9-Me), 2.46 and 2.86 (2 H, AB part of ABX, $J_{3,3'}$ 13.7 Hz, 3- and 3'-H), 3.36 (1 H, m, 4-H), 3.62 and 3.64 (each 1 H, s, 1- and 1'-H), 3.79 (3 H, s, OMe), and 6.58 and 6.80 (2 H, br AB, $J_{6,8}$ 2.0 Hz, ArH); irradiation at δ 2.44 sharpened the AB system, and irradiation at δ 3.36 collapsed the 4-Me signal to a singlet, $\nu_{max.}$ (CCl_4) 1 727 (C=O) and 1 622 (C=C) cm^{-1} .

7-Methoxy-4,9-dimethyldibenzofuran-2-ol (6).—The dibenzofuranone (15) (287 mg) and 10% palladium–charcoal (0.5 g) were heated under reflux in diphenyl ether (5 ml) under dry nitrogen for 30 min. The mixture was diluted with ether and filtered through Kieselguhr. The solvents were removed from the filtrate by steam distillation. The residue crystallized from dichloromethane–light petroleum (charcoal) as needles (133 mg) of the *dibenzofuranol* (6), m.p. 156–157 °C (Found: C, 74.6; H, 5.9%; M^+ , 242. $C_{15}H_{14}O_3$ requires C, 74.35; H, 5.8%; M , 242); $\delta(CDCl_3, 90\text{ MHz})$ 2.50 and 2.65 (each 3 H, s, $W_{1,3}$ 1.9 Hz, 4- and 9-Me), 3.86 (3 H, s, OMe), 4.80 (1 H, s, D_2O exchangeable OH), 6.67 and 6.91 (2 H, br AB, $J_{6,8}$ 2.0 Hz, 8- and 6-H), and 6.67 and 7.17 (2 H, br AB, $J_{1,3}$ 2.5 Hz, 3- and 1-H); irradiation at δ 2.50 sharpened the AB system due to H-1,3 and irradiation at δ 2.65 sharpened the AB system due to H-6,8; $\lambda_{max.}$ 209, 227, 244, 267, 296, and 317 nm (ϵ 21 600, 23 300, 12 800, 12 800, 12 300, and 5 100). On methylation as before this gave the methyl ether (5) as prisms (from methanol), m.p. and mixed m.p. 119–120 °C; identical (mass and n.m.r. spectra and R_F values in three solvent systems) with the sample prepared previously (Found: C, 74.95; H, 6.15. Calc. for $C_{16}H_{16}O_3$: C, 75.0; H, 6.3%).

Ultraviolet Irradiation of 2,7,9-Trichloro-3-hydroxy-8-methoxy-1,6-dimethyldibenzo[b,e][1,4]dioxepin-11-one (21).—The depsidone (21) (50 mg) in benzene (150 ml) was irradiated for 4 h. The n.m.r. spectrum of the material obtained on removal of the solvent was identical with that of the starting depsidone.

Photolysis of 3',5,5'-Trichloro-4',6-dimethoxy-4,6'-dimethylspiro[benzofuran-2,1'-cyclohexa-3',5'-diene]-2',3(2H)-dione (2).—(a) The grisadienedione (2) (90 mg) in benzene (150 ml) was irradiated for 1 h. This gave 1,3,8-trichloro-2,7-dimethoxy-4,9-dimethyldibenzofuran (9) (56 mg) as needles (from chloroform–methanol), m.p. and mixed m.p. 179–180 °C, identical (mass and n.m.r. spectra) with the sample prepared earlier.

(b) The grisadienedione (2) (14 mg) in absolute methanol (20 ml) was irradiated for 30 min. The n.m.r. spectrum of the residue obtained on removal of the solvent showed only the presence of the dibenzofuran (9).

Photolysis of 5'-Chloro-6-hydroxy-4'-methoxy-3',4,6'-trimethylspiro[benzofuran-2,1'-cyclohexa-3',5'-diene]-2',3(2H)-dione (3).—The grisadienedione (3) (78 mg) was irradiated in benzene (40 ml) for 2.75 h. This gave 7-chloro-8-methoxy-1,6,9-trimethyldibenzofuran-3-ol (11) (20 mg) as prisms (from chloroform–light petroleum), m.p. 183–185 °C (Found: M^+ , 290.070 3. $^{12}C_{16}^{1}H_{15}^{35}Cl^{16}O_3$ requires M , 290.071 0); $\delta(CDCl_3, 90\text{ MHz})$ 2.55, 2.80, and 2.84 (each 3 H,

s, Me), 3.82 (3 H, s, OMe), 5.23br (1 H, OH), 6.60 and 6.86 (2 H, br AB, $J_{2,4}$ 2.0 Hz, 2- and 4-H); irradiation at δ 2.84 sharpened the AB system; $\lambda_{max.}$ 220, 232, 259, 267, 299, and 311 nm (ϵ 30 000, 29 000, 9 100, 13 200, 21 100, and 21 500).

Photolysis of 5'-Chloro-6-hydroxy-4'-methoxy-3',4,6',7-tetramethylspiro[benzofuran-2,1'-cyclohexa-3',5'-diene]-2',3(2H)-dione (4).—Photolysis of the grisadienedione (4) (100 mg) in benzene (100 ml) for 2 h gave 7-chloro-8-methoxy-1,4,6,9-tetramethyldibenzofuran-3-ol (12) (65 mg) as prisms (from dichloromethane–light petroleum), m.p. 190.5–192.5 °C (Found: M^+ , 304.090 0. $^{12}C_{17}^{1}H_{17}^{35}Cl^{16}O_3$ requires M , 304.086 6); $\delta(CDCl_3, 60\text{ MHz})$ 2.37 and 2.52 (each 3 H, s, Me), 2.72 (6 H, s, 2 \times Me), 3.73 (3 H, s, OMe), and 6.54 (1 H, s, ArH); $\lambda_{max.}$ 222, 237, 260, 269, 298, 308, and 315sh nm (ϵ 31 100, 29 600, 8 300, 11 400, 18 700, 18 800, and 12 700). On methylation in the usual way this gave 3-chloro-2,7-dimethoxy-1,4,6,9-tetramethyldibenzofuran as felted needles (from dichloromethane–light petroleum), m.p. 151.5–153 °C (Found: M^+ , 318.101 4. $^{12}C_{18}^{1}H_{19}^{35}Cl^{16}O_3$ requires M , 318.102 3); $\delta(CDCl_3, 60\text{ MHz})$ 2.33, 2.51, 2.73, and 2.80 (each 3 H, s, Me), 3.76 and 3.82 (each 3 H, s, OMe), and 6.52 (1 H, s, ArH).

Hydrogenolysis of 3-Chloro-2,7-dimethoxy-1,4,6,9-tetramethyldibenzofuran.—This chloro-compound (30 mg) was hydrogenolysed by the method above. The product, 2,7-dimethoxy-1,4,6,9-tetramethyldibenzofuran (17) (21 mg) formed prisms (from methanol), m.p. 127–128.5 °C (lit.,⁴ 126–127 °C); $\delta(CDCl_3, 80\text{ MHz})$ 2.39, 2.53, 2.72, and 2.89 (each 3 H, s, Me), 3.86 and 3.91 (each 3 H, s, OMe), 6.63 and 6.80 (each 1 H, s, ArH); $\lambda_{max.}$ 219, 235, 260, 270, 297, 315, and 327 nm (ϵ 33 500, 31 800, 8 900, 12 000, 18 100, 5 700, and 2 900).

Photolysis of 6-Hydroxy-4'-methoxy-4,6'-dimethylspiro[benzofuran-2,1'-cyclohexa-3',5'-diene]-2',3(2H)-dione (16).—The grisadienedione (16) (110 mg) in benzene (50 ml) was irradiated for 9 h. This gave 8-methoxy-1,6-dimethyldibenzofuran-3-ol (7) (12 mg) as prisms (from dichloromethane–light petroleum), m.p. 149.5–151.5 °C (Found: M^+ , 242.092 2. $^{12}C_{15}^{1}H_{14}^{16}O_3$ requires M , 242.094 3); $\delta(CDCl_3, 80\text{ MHz})$ 2.54 and 2.70 (each 3 H, s, Me), 3.89 (3 H, s, OMe), 4.92 (1 H, s, OH), 6.59 and 6.85 (2 H, br AB, $J_{2,4}$ 2.0 Hz, 2- and 4-H), and 6.78 and 7.23 (2 H, br AB, $J_{6,8}$ 2.5 Hz, 6- and 8-H); $\lambda_{max.}$ 211, 229, 245inf, 259, 306, and 319 nm (ϵ 24 200, 26 700, 15 800, 12 700, 14 900, and 8 200). On methylation as before this gave the methyl ether (5) as prisms (from aqueous methanol), m.p. and mixed m.p. 119–120 °C, identical with the sample prepared previously.

Photolysis of 3',5,5'-Trichloro-2',6-dihydroxy-4,6'-dimethylspiro[benzofuran-2,1'-cyclohexa-2',5'-diene]-3(2H),4'-dione (18).—The grisadienedione (18) (100 mg) in benzene (100 ml) was irradiated for 4.5 h. Preparative t.l.c. gave 1,3,8-trichloro-4,9-dimethyldibenzofuran-2,7-diol (19) (9.6 mg) as needles (from chloroform–light petroleum), m.p. 219–222 °C (Found: M^+ , 329.963 0. $^{12}C_{14}^{1}H_9^{35}Cl_3^{16}O_3$ requires M , 329.961 7); $\delta(CDCl_3-CD_3SOCD_3, 60\text{ MHz})$ 2.50 and 3.02 (each 3 H, s, Me), and 6.98 (1 H, s, ArH). A slower band gave the starting material (80 mg).

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