

The Synthesis of Dihydrofurobenzodioxins by Reaction of Tetrachloro-1,2-benzoquinone with Some 2,3-Diphenylfurans

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The synthesis of some alkyl-2,3-diphenylfurans and their reaction with tetrachloro-1,2-benzoquinone to afford dihydrofurobenzodioxins are described. 2,3-Diphenyl-, 2,3,5-triphenyl-, and tetraphenyl-furan react in the same manner by a Diels–Alder process utilising the hetero-diene part of the quinone. Steric rather than electronic factors are important in determining which double bond of the furan is utilised as the dienophile.

FURANS have previously been used as the dienophile portion in Diels–Alder reactions with 1,2-benzoquinones.¹ Early work established that tetrachloro-1,2-benzoquinone, a quinone with a high redox potential, reacts with benzofuran to yield a benzodioxin (1).² Subsequently it was demonstrated that furan, 2-methyl-

furan, and 2,5-diphenylfuran reacted similarly.³ Other work⁴ has shown that when alternative reactions are possible, *e.g.* reaction at a vinyl side chain or on the furan nucleus, then reaction takes place on the furan. However it is not yet clear whether electronic or steric factors are predominant in determining which double bond of the furan was preferred.

It is tempting to consider the addition of benzo-

¹ W. M. Horspool, *Quart. Rev.*, 1969, **23**, 204.

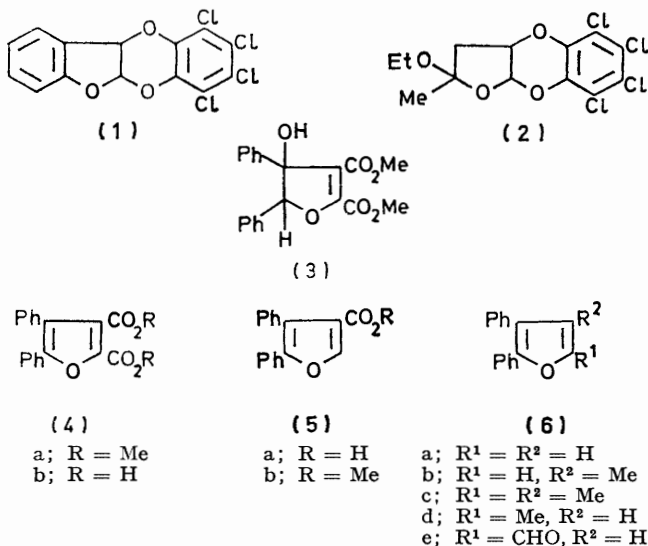
² L. Horner and H. Merz, *Annalen*, 1950, **570**, 89.

³ W. M. Horspool, J. M. Tedder, and Z. ud Din, *J. Chem. Soc. (C)*, 1969, 1694.

⁴ N. Latif, N. Saddik, and F. Mikhail, *Tetrahedron Letters*, 1969, 3987.

quinone to a furan as a Diels–Alder reaction and consequently as a concerted process. However the possibility that the high redox potential quinones (tetrachloro-1,2-benzoquinone ⁵ 0.83 mV, 1,2-benzoquinone ⁵ 0.79 mV) might react as electrophiles with comparatively electron-rich furan systems must also be considered. Such a suggestion has some foundation in that the reaction of 1,2-benzoquinone with 2-methylfuran in chloroform (1% ethanol as stabiliser) gives benzodioxins with incorporation of the ethanol.³ Such a product (2) could only be formed by a two-step ionic mechanism. The present report deals with attempts to show which mechanism is operative.

For the purpose of the investigation we required several 2,3-diphenylfurans. Only three of these were known, 2,3-diphenyl-, 2,3,5-triphenyl-, and tetraphenyl-furan. The route to the first of this group proved useful for the preparation of intermediates which could be used for the synthesis of the alkyl-2,3-diphenylfurans, and so considerable time was spent on this particular synthetic scheme.⁶ The route chosen was one⁶ which involved the base-catalysed addition of benzoin to dimethyl acetylenedicarboxylate to give the hydroxydihydrofuran (3). The conditions used for the dehydration of this compound to the furan (4a) had



to be more vigorous than those reported.⁶ The second modification used in the synthesis was the application of a copper oxide-catalysed double decarboxylation of the diacid (4b) previously described for the conversion of imidazole-4,5-dicarboxylic acid into imidazole.⁷ This method gave a good yield of the furan without the need for the two separate decarboxylation processes described previously. The product (5a) of single decarboxylation was used for the synthesis of 3-methyl-4,5-diphenylfuran (6b). The acid was esterified by the conventional route

and mixed hydride reduction of the ester (5b) yielded the desired furan (6b). A similar mixed hydride reduction was employed for the transformation of the diacid (4b) into 2,3-dimethyl-4,5-diphenylfuran (6c). The synthesis of the other methyl-diphenylfuran (6d) was achieved by a Wolff–Kishner conversion of the 2-aldehyde (6e).

TABLE I
N.m.r. spectral details of 2,3-diphenylfuran and alkylated derivatives

Furan (6a)	Chemical shifts (τ ; CDCl ₃)		
	Aryl groups	Ring protons	Alkyl groups
	2.65–2.90(10H)	2.57 (d, <i>J</i> 2 Hz, 1H)	Ref. 6
		3.63 (d, <i>J</i> 2 Hz, 1H)	
(6b)	2.66–3.13(11H)	Under aryl proton signals	8.09 (d, <i>J</i> 1 Hz, 3H)
(6d)	2.46–3.10(10H)	4.01 (s, 1H)	7.78 (s, 3H)
(6c)	2.59–3.08(10H)		7.74 (s, 3H) 8.22 (s, 3H)

The new furans exhibited typical n.m.r. spectra; Table I shows that the α -protons all resonate at lower frequencies than the β -protons. The typical line positions for the group are shown for 2,3-diphenylfuran (6a) but in accord with other results⁸ the exact position of the resonances depends to a large extent on the type of substituent on the ring. In addition the coupling between the 3-methyl group and the 4-proton in the furan (6d) is measurable (*ca.* 1 Hz), whereas the coupling between the 3-methyl group and the 2-proton in the furan (6b) results only in broadening of the methyl singlet. This observation also has a precedent.⁹

Synthesis of Furan–Tetrachloro-1,2-benzoquinone Adducts.—The reaction of 2,3-diphenylfuran (6a) with tetrachloro-1,2-benzoquinone in refluxing benzene afforded a single adduct in good yield. The identity of this product (7a) was confirmed mainly by n.m.r. spectroscopy. In particular the shift of the two furan ring protons to a more shielded environment (from τ 2.57 and 3.63 to 3.51 and 4.05) confirms that the addition has taken place to the unsubstituted double bond. In addition the coupling constant of 6.9 Hz between the two hydrogen atoms is the same as that measured for the furan–tetrachloro-1,2-benzoquinone adduct.³ The stereochemistry of the ring junction in this molecule was assumed to be *cis* following consideration of molecular models. Unfortunately catalytic hydrogenation, which would have confirmed the point for adduct (7a) and had been used previously by us,³ destroyed the molecule.

No evidence is available concerning the concertedness of the reaction, although previous work has demonstrated³ that under certain conditions the reaction of 1,2-benzoquinone with furans in chloroform–ethanol

⁵ L. Horner and E. Geyer, *Chem. Ber.*, 1965, **98**, 2009.

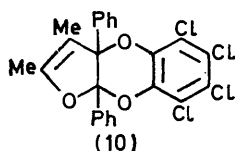
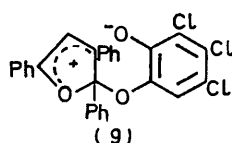
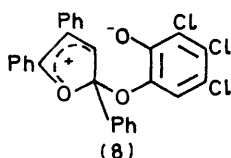
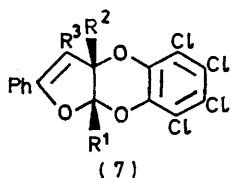
⁶ A. Padwa and R. Hartman, *J. Amer. Chem. Soc.*, 1966, **88**, 1518.

⁷ H. R. Snyder, R. G. Handrick, and L. A. Brooks, *Org. Synth.*, 1942, **22**, 65.

⁸ R. F. M. White, 'Physical Methods in Heterocyclic Chemistry', ed. A. R. Katritzky, Academic Press, New York, vol. II, 1963.

⁹ R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216, 905; J. B. Leane and R. E. Richards, *Trans. Faraday Soc.*, 1959, **55**, 518.

gives adducts [*e.g.* (2)] incorporating the ethanol *via* a two step reaction involving carbonium ions. If such a species were involved in the addition described herein it should be possible to use a molecule where the difference between a concerted process, strongly influenced by steric factors, and a two step mechanism, where electronic factors are the controlling features, would be obvious. The molecule chosen was 2,3,5-triphenylfuran; if a two step addition were involved with minimal steric interference then two zwitterionic intermediates (8) and (9) are possible, with zwitterion (9) being more stable owing to interaction with two



- a; R¹ = R² = H, R³ = Ph
 b; R¹ = R² = Ph, R³ = H
 c; R¹ = Ph, R² = R³ = H
 d; R¹ = Me, R² = H, R³ = Ph
 e; R¹ = H, R² = Me, R³ = Ph
 f; R¹ = R² = R³ = Ph
 g; R¹ = R² = Me, R³ = Ph

phenyl groups. The reaction of 2,3,5-triphenylfuran with tetrachloro-1,2-benzoquinone in benzene gave one product, identified as the adduct (7b). The assignment of structure was based again on the n.m.r. spectrum, which showed that the single furan ring proton was relatively shielded [τ 4.1 *cf.* 4.31 for the proton in a similar but not identical environment in adduct (7c)³]. It was therefore concluded, since addition had taken place exclusively on the 3,4-double bond of the furan, that steric and not electronic factors play the dominant role. Successful additions of tetrachloro-1,2-benzoquinone to 2-methyl- and 3-methyl-4,5-diphenylfurans to afford the adducts (7d) and (7e), respectively, help to reinforce this conclusion. The n.m.r. data for the latter two adducts again show, from the relatively shielded environment of the methyl groups and the furan ring hydrogen atoms, that addition has taken place to the less substituted double bond. The addition of the quinone to tetraphenylfuran also gave an adduct (7f).

Only with 2,3-dimethyl-4,5-diphenylfuran is this rule violated. The reaction of this compound with the quinone furnished two adducts (in the ratio 1 : 1 based on n.m.r. integrals), which could only be separated by fractional crystallisation. One of the major differences between the adducts was in the chemical shifts of the methyl groups, one having absorptions at τ 8.00 and

8.15 and the other at 8.03 and 8.20. However the difference was insufficient evidence for definite assignment of the resonances to either of the two possible structures (7g) and (10). Catalytic hydrogenation was unsuccessful and only brought about decomposition; u.v. spectroscopy was eventually used to solve the

TABLE 2

Adduct	Chemical shifts (τ ; CDCl ₃)		
	Aryl groups	Ring hydrogens	Alkyl groups
(7a)	2.60—2.90(m, 10H)	3.78(2H, dd, $\Delta\nu_{AB}$ 32.5, J 6.9 Hz)	
(7b)	2.15—2.75(m, 15H)	4.17(s, 1H)	
(7d)	2.57—3.04(m, 10H)	4.53(s, 1H)	8.07(s, 3H)
(7e)	2.60—2.87(m, 10H)	3.91(s, 1H)	8.21(s, 3H)
(7f)	2.26(m, 5H), 2.64(m, 5H), 3.02(m, 5H), 3.39(m, 5H)		
(7g)	2.40—2.90(m, 10H)		8.03(s, 3H), 8.20(s, 3H)
(10)	2.25—3.10(m, 10H)		8.00(s, 3H), 8.15(s, 3H)

problem. All the compounds so far synthesised had u.v. maximum at *ca.* 290 nm (ϵ *ca.* 8×10^3). This absorption is presumably the sum of the tetrachlorocatechyl and diphenyl enol ether contributions. Only structure (7g) has both features and can be assigned to the adduct with the higher extinction coefficient. This enables us to suggest that the two adducts from the 2,3-dimethyl-4,5-diphenylfuran-tetrachloro-1,2-benzoquinone reaction be assigned as follows: structure (7g) is that with n.m.r. absorptions at τ 8.03 and 8.20 and structure (10) is that with absorptions at τ 8.00 and 8.15.

EXPERIMENTAL

I.r. spectra were recorded for liquid films or Nujol mulls with a Perkin-Elmer 137 spectrometer. U.v. spectra were measured with a Unicam SP 800 instrument and n.m.r. spectra for carbon tetrachloride or deuteriochloroform solutions (tetramethylsilane as internal standard) with a Perkin-Elmer R10 60 MHz spectrometer. Chromatography was carried out with Spence grade H alumina and the light petroleum used had b.p. 40—60°. 2,3,5-Triphenylfuran, m.p. 93—94° (lit.,¹⁰ m.p. 92°) and tetraphenylfuran, m.p. 173—174° (lit.,¹¹ m.p. 175°), were prepared by reported methods.

2,3-Diphenylfuran.—This was prepared by modification of the method of Padwa and Hartman⁶ as follows.

(a) *Dehydration of dimethyl 4,5-dihydro-4-hydroxy-4,5-diphenylfuran-2,3-dicarboxylate*. The hydroxydihydrofuran (28 g) was rapidly dehydrated by refluxing for 2 h in methanol (300 ml) and conc. sulphuric acid (20 ml). Pouring on ice, filtration, and washing with water gave the desired furan, m.p. 87—89° (from methanol) (lit.,⁶ m.p. 86—88°).

(b) *Double decarboxylation of 4,5-diphenylfuran-2,3-di-*

¹⁰ A. Smith, *J. Chem. Soc.*, 1890, 645.

¹¹ S. Patai, Y. Halpern, and M. Michman, U.S.P. 3,359,284 (*Chem. Abs.*, 1968, 69, 10,347).

carboxylic acid. The diacid (7.0 g) and copper oxide (0.25 g) were intimately mixed and the mixture was heated in a flask with a Bunsen flame until evolution of gas had ceased. The mixture was cooled and the organic material was extracted. The residue obtained on evaporation was chromatographed on alumina. Light petroleum eluted 2,3-diphenylfuran (2.74 g, 55%) as an oil. The product was purified by distillation and had b.p. 180–181° at 1 mmHg (lit.,⁶ b.p. 173–174° at 0.8 mmHg).

Methyl 4,5-Diphenylfuran-3-carboxylate.—4,5-Diphenylfuran-3-carboxylic acid⁶ (5.0 g) was dissolved in methanol (150 ml) and conc. sulphuric acid (10 ml) was added. The mixture was heated at reflux for 5 h, cooled to room temperature, poured into sodium hydrogen carbonate solution, and extracted with ether. The ether layer was washed thoroughly, dried (Na₂SO₄), filtered, and evaporated to dryness to give a pale yellow crystalline solid (5.1 g). This was recrystallised from light petroleum–cyclohexane to afford the *ester*, needles, m.p. 92–93°, ν_{\max} (Nujol) 1745 cm⁻¹ (C=O), τ (CCl₄) 1.88 (s, 1H), 2.58–2.85 (m, 10H), and 6.32 (s, 3H) (Found: C, 78.0; H, 5.0. C₁₈H₁₄O₃ requires C, 77.7; H, 5.0%).

3-Methyl-4,5-diphenylfuran (6b).—Aluminium chloride (60 g) was dissolved in dry ether (150 ml) under nitrogen. This solution was added slowly to a stirred, ice-cold, solution of lithium aluminium hydride (6.84 g) in dry ether (140 ml). Methyl 4,5-diphenylfuran-3-carboxylate (5.8 g) in dry ether (200 ml) was added and the resultant mixture was refluxed for 7 days. It was then cooled in ice, acidified carefully with dilute hydrochloric acid (0.1M), and extracted with ether. The ether layer was washed with water and sodium hydrogen carbonate solution, dried (MgSO₄), filtered, and evaporated to dryness. The resultant yellow oil was chromatographed on alumina. Benzene eluted *3-methyl-4,5-diphenylfuran* (3.63 g, 74%), b.p. 164° at 1.5 mmHg, ν_{\max} (film) 1604, 1510, 1490, 1460, 1080, 950, 930, 780, and 710 cm⁻¹ (Found: C, 86.6; H, 6.6. C₁₇H₁₄O requires C, 87.2; H, 6.0%). The oil eventually crystallised (at 0°) to give a pale yellow solid, m.p. 57–66°.

2,3-Dimethyl-4,5-diphenylfuran (6c).—Aluminium chloride (15.0 g) was dissolved (slurried) in dry ether (450 ml). This was then added slowly with stirring to an ice-cold solution of lithium aluminium hydride (17.1 g) in dry ether (350 ml). 4,5-Diphenylfuran-2,3-dicarboxylic acid (8.0 g) was then added as a suspension in dry ether (100 ml) and the resulting mixture was refluxed for 6 days. The mixture was cooled in ice and acidified carefully with cold dilute hydrochloric acid (0.1M). The ether layer was separated and washed with water and sodium hydrogen carbonate solution, dried (MgSO₄), filtered, and evaporated to give a dark brown oil. This oil was chromatographed on alumina (benzene as eluant). *2,3-Dimethyl-4,5-diphenylfuran* (5.14 g, 86%) was distilled; b.p. 132° at 0.4 mmHg. The distillate crystallised to give the furan as a pale yellow solid, m.p. 57–64°, ν_{\max} 1600, 1510, 1460, 1260, 1080, 960, 770, and 710 cm⁻¹ (Found: C, 86.8; H, 6.8. C₁₈H₁₆O requires C, 87.1; H, 6.5%). This material slowly decomposed to an unidentified green oil.

2-Methyl-4,5-diphenylfuran (6d).—4,5-Diphenyl-2-furaldehyde (7.4 g)⁶ was dissolved in diethylene glycol (66 ml) and hydrazine hydrate (21.5 ml; 100%). The mixture was refluxed for 1.5 h, then cooled, and potassium hydroxide (7.4 g) was added.¹² This mixture was refluxed for 20 min and then excess of hydrazine was removed under reduced pressure. The remaining mixture was heated

for a further 3 h at 195–200°, cooled, and diluted with water, and the organic material was extracted into ether. The ether layer was washed with water, dried, filtered, and evaporated to dryness. The resulting yellow oil was chromatographed on alumina. Light petroleum slowly eluted *2-methyl-4,5-diphenylfuran* (5.4 g, 77%), b.p. 168° at 1 mmHg, as an oil, ν_{\max} (film) 1605, 1560, 1500, 1450, 1135, 1080, 960, 770, and 720 cm⁻¹ (Found: C, 86.6; H, 6.6. C₁₇H₁₄O requires C, 87.2; H, 6.0%).

2,3-Diphenylfuran-Tetrachloro-1,2-benzoquinone Adduct (7a).—2,3-Diphenylfuran (2.74 g) and tetrachloro-1,2-benzoquinone (3.2 g) were dissolved in dry benzene (40 ml) and heated for 4 h under nitrogen. Work-up gave a red oil which crystallised on addition of cyclohexane. Recrystallisation from cyclohexane gave pale beige crystals of *5,6,7,8-tetrachloro-3a,9a-dihydro-2,3-diphenylfuro[2,3-b]-[1,4]benzodioxin* (7a) (2.8 g, 47%), m.p. 140–142°, ν_{\max} 1640, 1560 (C=C), 1060, 1030, and 1020 (C–O–C) cm⁻¹, λ_{\max} (MeOH) 295 nm (ϵ 8700) (Found: C, 57.9; H, 3.3; Cl, 30.9. C₂₂H₁₂Cl₄O₃ requires C, 56.7; H, 2.6; Cl, 30.5%).

2,3,5-Triphenylfuran-Tetrachloro-1,2-benzoquinone Adduct (7b).—2,3,5-Triphenylfuran (3.0 g) and tetrachloro-1,2-benzoquinone (2.5 g) were dissolved in dry benzene (50 ml) and the mixture was refluxed for 4.5 h as in previous experiments. Removal of the solvent gave a solid which was chromatographed on alumina. Benzene eluted a pale beige solid which was recrystallised from benzene–light petroleum to give *5,6,7,8-tetrachloro-3a,9a-dihydro-2,3,9a-triphenylfuro[2,3-b]-[1,4]benzodioxin* (7b) (2.6 g, 48%), m.p. 163–164°, ν_{\max} (Nujol) 1650, 1605, 1580 (C=C), 1160, 1030, and 1000 (C–O–C) cm⁻¹, λ_{\max} (MeOH) 300 nm (ϵ 6730) (Found: C, 62.1; H, 3.2; Cl, 26.0. C₂₅H₁₆Cl₄O₃ requires C, 62.1; H, 3.0; Cl, 26.3%).

2-Methyl-4,5-diphenylfuran-Tetrachloro-1,2-benzoquinone Adduct (7d).—2-Methyl-4,5-diphenylfuran (1.5 g) and tetrachloro-1,2-benzoquinone (1.58 g) were dissolved in dry benzene (40 ml). Nitrogen was bubbled through the solution for 0.5 h and then the solution was refluxed for 4 h under a positive pressure of nitrogen. The solvent was removed under vacuum to afford a red oil which was chromatographed on alumina. Benzene eluted an oil (2.50 g, 81%) which rapidly crystallised after removal of the solvent and was recrystallised from benzene–light petroleum to afford crystals of *5,6,7,8-tetrachloro-3a,9a-dihydro-9a-methyl-2,3-diphenylfuro[2,3-b]-[1,4]benzodioxin* (7d), m.p. 161–162°, ν_{\max} (Nujol) 1650, 1605, 1610 (C=C), 1100, 1080, and 1010 (C–O–C) cm⁻¹, λ_{\max} (MeOH) 292 nm (ϵ 11,400) (Found: C, 57.3; H, 3.0; Cl, 29.6. C₂₃H₁₄Cl₄O₃ requires C, 57.5; H, 2.9; Cl, 29.6%).

3-Methyl-4,5-diphenylfuran-Tetrachloro-1,2-benzoquinone Adduct (7e).—3-Methyl-4,5-diphenylfuran (1.5 g) and tetrachloro-1,2-benzoquinone (1.58 g) were dissolved in dry benzene (50 ml) and treated for 4½ h as described above. The red oil obtained after removal of the solvent was chromatographed on alumina. Benzene eluted a yellow band which yielded a pale yellow solid. This was crystallised from benzene–light petroleum to give pale beige crystals of *5,6,7,8-tetrachloro-3a,9a-dihydro-3a-methyl-2,3-diphenylfuro[2,3-b]-[1,4]benzodioxin* (7e) (2.2 g, 71%), m.p. 172–172.5°, ν_{\max} (Nujol) 1660, 1604, 1570 (C=C), 1090, 1070, 1010, and 990 (C–O–C) cm⁻¹, λ_{\max} (MeOH) 282 nm (ϵ 10,500) (Found: C, 58.1; H, 3.2; Cl, 29.9. C₂₃H₁₄Cl₄O₃ requires C, 57.5; H, 2.9; Cl, 29.6%).

¹² H. Min-Lon, C. Tung-Shun, K. Tu-Shin, and C. Wei-Kan, *Hua Hseuh Hseuh Pao*, 1961, **27**, 1 (*Chem. Abs.*, 1963, **59**, 11,480c).

Tetraphenylfuran-Tetrachloro-1,2-benzoquinone Adduct (7f).—Tetraphenylfuran (3.0 g) and tetrachloro-1,2-benzoquinone (1.98 g) were heated under reflux in dry benzene (50 ml) for 4 h. Work-up gave a pale yellow solid which was crystallised from benzene-light petroleum to give 5,6,7,8-tetrachloro-3a,9a-dihydro-2,3,3a,9a-tetra-phenylfuro[2,3-b][1,4]benzodioxin (7f) (3.5 g, 70%), m.p. 202–203°, ν_{\max} (Nujol) 1130, 1060, 1040, and 1010 (C–O–C) cm^{-1} , λ_{\max} (MeOH) 216 (ϵ 67,300) and 230sh nm (with long tail) (Found: C, 66.7; H, 3.5; Cl, 22.5. $\text{C}_{34}\text{H}_{26}\text{Cl}_4\text{O}_3$ requires C, 66.0; H, 3.2; Cl, 23.0%).

Reaction of 2,3-Dimethyl-4,5-diphenylfuran with Tetrachloro-1,2-benzoquinone.—2,3-Dimethyl-4,5-diphenylfuran (4.20 g) was dissolved in dry benzene (80 ml) and tetrachloro-1,2-benzoquinone (4.17 g) was added. This solution was heated at reflux under nitrogen for 5 h, cooled, and evaporated under reduced pressure. The residual red oil was chromatographed on alumina. Light petroleum ether eluted unchanged furan (1.75 g) followed by a yellow viscous oil (5.37 g). The n.m.r. spectrum of this material indicated that it was a 1:1 mixture of two compounds (the four singlets at τ 8.00, 8.03, 8.15, and 8.20). These compounds, which are presumed to be isomers, could not be separated by chromatography, but fractional crystallisation from benzene-petroleum ether did afford separation.

Fraction (a) was 5,6,7,8-tetrachloro-3a,9a-dihydro-3a,9a-

dimethyl-2,3-diphenylfuro[2,3-b][1,4]benzodioxin (7g) (2.0 g), m.p. 123–124.5°, ν_{\max} (Nujol) 1660, 1570 (C=C), 1090, 1075, and 1010 (C–O–C) cm^{-1} , λ_{\max} (MeOH) 292 nm (ϵ 8250), τ (CDCl_3) 2.4–2.9 (m, 10H), 8.03 (s, 3H), and 8.20 (s, 3H) (Found: C, 58.7; H, 3.5; Cl, 28.8. $\text{C}_{24}\text{H}_{16}\text{Cl}_4\text{O}_3$ requires C, 58.3; H, 3.2; Cl, 28.7%).

Fraction (b) was 5,6,7,8-tetrachloro-3a,9a-dihydro-2,3-dimethyl-3a,9a-diphenylfuro[2,3-b][1,4]benzodioxin (10) (1.5 g), m.p. 131–132.5°, ν_{\max} (Nujol) 1605 (C=C) 1100, 1060, 1000, and 990 (C–O–C) cm^{-1} , λ_{\max} (MeOH) 294 nm (ϵ 7.36×10^3), τ (CDCl_3) 2.25–3.10 (m, 10H), 8.00 (s, 3H), and 8.15 (s, 3H) (Found: C, 58.5; H, 3.4; Cl, 28.7. $\text{C}_{24}\text{H}_{16}\text{Cl}_4\text{O}_3$ requires C, 58.3; H, 3.2; Cl, 28.7%).

Catalytic Reduction of Dihydrofurobenzodioxin (7g).—The adduct (0.31 g) in ethyl acetate (25 ml) containing 30% palladium-charcoal (0.1 g) was hydrogenated (uptake 30 ml in 30 min). Work-up gave an oil whose n.m.r. spectrum indicated that hydrogenolysis as well as hydrogenation had taken place. No attempt was made to separate the complex mixture.

Catalytic Reduction of Dihydrofurobenzodioxin (10).—Reduction of this adduct as above caused breakdown of the molecule.

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