

Palladium-catalysed Dibenzofuran Synthesis by Dehydrogenative Ring Closure

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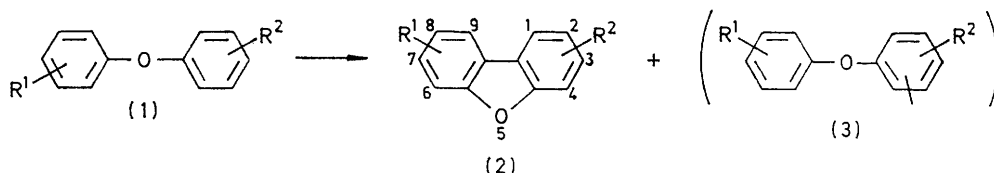
Diphenyl ethers readily undergo intramolecular and intermolecular dehydrogenative coupling in the presence of a catalytic quantity of palladium acetate under oxygen pressure to give dibenzofurans and dimers, respectively. The addition of an inert solvent to this system increases the yield of dibenzofurans relative to dimers. Product ratios and an isotope effect in competitive coupling suggest that dibenzofuran is formed by a stepwise coupling mechanism similar to the intermolecular coupling of aryl compounds. The preparation of dibenzofurandicarboxylic acids and the regeneration of the palladium catalyst are described.

THE oxidative coupling of aryl compounds with palladium chloride and sodium acetate in acetic acid solution at 100 °C has been reported.¹ The effect of oxygen pressure on the coupling in the system benzene-palladium acetate-acetic acid has also been studied: acetoxylation was inhibited under oxygen pressure, although phenyl acetate was formed in the absence of oxygen.² Methylated benzenes were readily oxidised with palladium acetate in trifluoroacetic acid to give products of nuclear coupling and aryl methylation.³ Aryl compounds react stoichiometrically with an equimolar quantity of palladium acetate to give coupling products. Iodobenzenes, however, form biaryls in the presence of a catalytic quantity of palladium acetate.⁴ Itatani *et al.* improved the dehydrogenative coupling reaction to bring about a remarkable increase in yield of biaryls in the absence of acetic acid at 150 °C under oxygen pressure.⁵ This procedure provided a new synthetic route to dibenzofurans from diphenyl ethers.⁶

catalysed cyclisation of arylbenzoquinones.⁹ Recently, the palladium-promoted cyclisation of diphenyl ethers was reported, in which 2 equiv. of palladium acetate and a reaction time of 24 h were required.¹⁰ In the absence of acetic acid, under oxygen pressure, however, we found that the coupling proceeded with a catalytic quantity of palladium acetate to give dibenzofuran in higher yields.⁶ We now deal with substituent effects in competitive reactions of diphenyl ethers and an isotope effect with a deuteriated diphenyl ether.

RESULTS AND DISCUSSION

Solvent Effect on Intra- and Inter-molecular Couplings.—The coupling reaction of diphenyl ethers (1) in the presence of a catalytic quantity of palladium acetate and acetylacetone under oxygen pressure gave dibenzofuran derivatives (2) (intramolecular coupling products) as well as dimers (3) (intermolecular coupling products) in good yields. *o*- and *m*-Substituted diphenyl



	R ¹	R ²
a;	H	H
b;	<i>p</i> -Me	<i>p</i> -Me
c;	<i>m</i> -Me	<i>p</i> -Me
d;	<i>o</i> -Me	<i>p</i> -Me
e;	H	<i>p</i> -NO ₂
f;	H	<i>o</i> -Pr ⁱ

	R ¹	R ²
a;	H	H
b;	8-Me	2-Me
c;	7-Me	2-Me
d;	6-Me	2-Me
e;	H	2-NO ₂
f;	H	4-Pr ⁱ

Previously, dibenzofurans had been prepared by ring closure of diazotised *ortho*-aminodiphenyl ethers,⁷ by dehydration of 2,2'-dihydroxybiphenyl,⁸ and from acid-

ethers were converted into dibenzofuran derivatives in lower yield than the *p*-substituted ones. Use of an appropriate amount of an inert solvent with the sub-

¹ R. van Helden and G. Verberg, *Rec. Trav. chim.*, 1965, **84**, 1263.

² J. M. Davidson and C. Triggs, *J. Chem. Soc. (A)*, 1968, 1331, 1324.

³ F. R. S. Clark, R. O. C. Norman, C. B. Thomas, and J. S. Willson, *J.C.S. Perkin I*, 1974, 1289.

⁴ F. R. S. Clark, R. O. C. Norman, and C. B. Thomas, *J.C.S. Perkin I*, 1975, 121.

⁵ H. Itatani and H. Yoshimoto, *J. Org. Chem.*, 1973, **38**, 76; *Chem. and Ind.*, 1971, 674; *Bull. Chem. Soc. Japan*, 1973, **46**, 2490.

⁶ A. Shiotani and H. Itatani, *Angew. Chem.*, 1974, **86**, 478; *Angew. Chem. Internat. Edn.*, 1974, **13**, 471.

⁷ (a) W. E. Parham and R. W. Strassburg, *J. Org. Chem.*, 1961, **26**, 4749; (b) D. F. DeTar and T. E. Whiteley, *J. Amer. Chem. Soc.*, 1957, **79**, 2498.

⁸ B. G. Pring and N. E. Stjernstrom, *Acta Chem. Scand.*, 1968, **22**, 681 (*Chem. Abs.*, 1968, **69**, 59,005h).

⁹ O. C. Musgrave and C. J. Webster, *J.C.S. Perkin I*, 1974, 2260, 2263.

¹⁰ B. Akermark, L. Ebersson, E. Jonsson, and E. Pettersson, *J. Org. Chem.*, 1975, **40**, 1365

stituted diphenyl ethers increased the yield of dibenzofurans and suppressed the formation dimers (Table 1).

TABLE 1

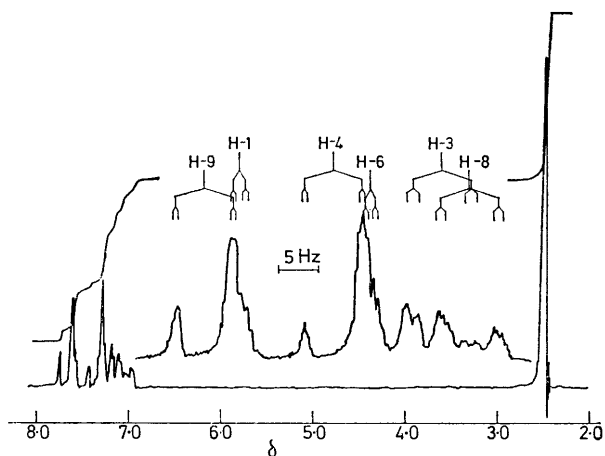
Coupling of diphenyl ethers (yields determined by g.l.c.) [starting material (15.0 g), Pd(OAc)₂ (0.15 mmol), acetylacetone (0.15 mmol), and O₂-N₂ (1:1) 50 kg cm⁻²; 5 h at 150 °C]

Starting material	Yields (%) †		Ratio
	Cyclised product	Dimers	
(1a)	8 090	3 710	2.0 : 1
(1a) *	10 400	2 530	4.1 : 1
(1b)	8 540	1 470	5.8 : 1
(1b) *	10 500	1 270	8.3 : 1
(1c)	730	330	2.2 : 1
(1c) *	9 220	590	15.6 : 1
(1d) *	330	110	3.0 : 1
(1f) *	390	120	3.2 : 1

* With addition of ethyleneglycol diacetate (5 ml). † Based on palladium acetate used.

The amounts of tarry by-products were reduced in the reaction of di-*p*-tolyl ether by the addition of solvent, with concurrent increase in the yield of 2,8-dimethyldibenzofuran (based on consumed di-*p*-tolyl ether). In the reaction of *m*-tolyl *p*-tolyl ether, with added ethylene glycol diacetate, the ratio of cyclised product to dimers was enhanced. Thus ethylene glycol diacetate plays an important role in the intramolecular coupling, and prevents formation of oxidation by-products. The *ortho*-substituted diphenyl ethers gave low yields of cyclised product.

Specificity of the Intramolecular Ring Closure.—*m*-Tolyl *p*-tolyl ether could in principle give either 2,7- and 2,9-dimethyldibenzofuran. Under our conditions, the 2,9-isomer was not obtained, but 2,7-isomer (2c) was isolated, and was characterised by ¹H n.m.r. spectroscopy (Figure). Probably the *m*-methyl group prevents



¹H N.m.r. spectrum of 2,7-dimethyldibenzofuran (in CCl₄)

2,9-isomer from forming. Bimesityl was not detected in the palladium-catalysed coupling of mesitylene.^{3,5}

In order to examine differences in reactivity between inter- and intra-molecular couplings, competitive re-

actions of diphenyl ether and its homologues were carried out (Table 2). The coupling reaction is suppressed by the nitro-group, but is somewhat facilitated by the methyl group as expected. The coupling reactions of benzophenone and 4,4'-dimethylbenzophenone give fluorenone and 3,6-dimethylfluorenone, respectively. However, the yield of fluorenone was only one hundredth of that of dibenzofuran in a competitive reaction (Table 2). Diphenyl sulphide, diphenyl sulphone, and *NN*-diphenylacetamide did not produce cyclised products under these conditions, but diphenylmethane gave fluorene.⁵ Accordingly, the facility of intramolecular ring closure decreases with respect to the bridging group connecting the two benzene rings in the

TABLE 2

Competitive reaction between diphenyl ether and its homologues

B ^a	Cyclised products (%) ^b		Ratio X _B : X _A
	X _B	X _A	
(1a)	5 260	5 260	1.00 : 1
(1e)	3 820	5 020	0.76 : 1
(1b)	4 890	4 650	1.05 : 1
Ph ₂ CO	64	6 710	0.0095 : 1

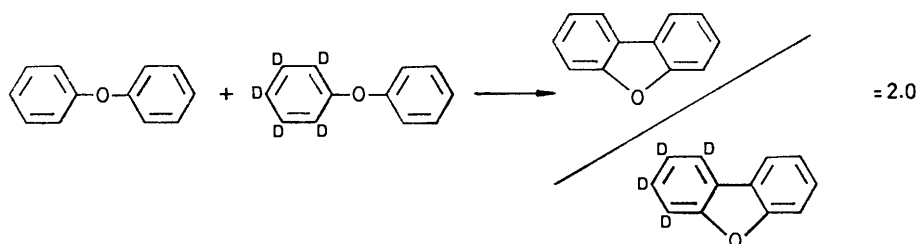
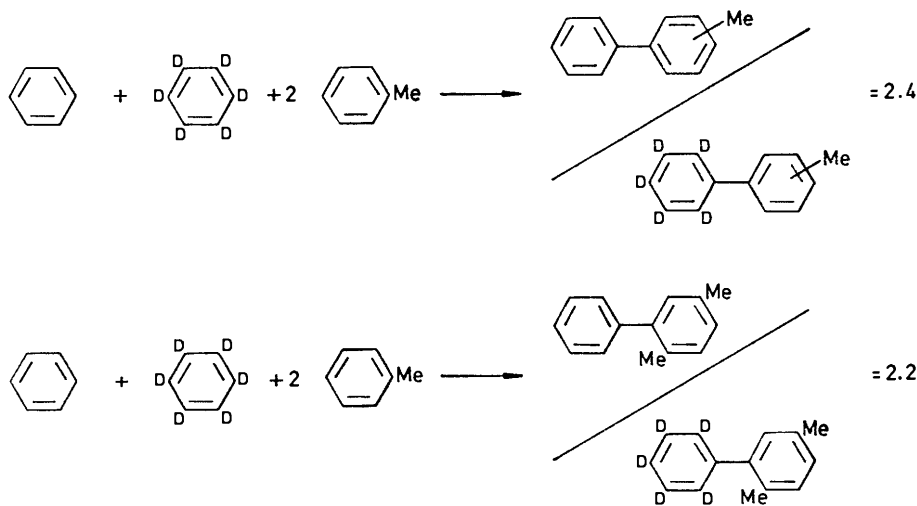
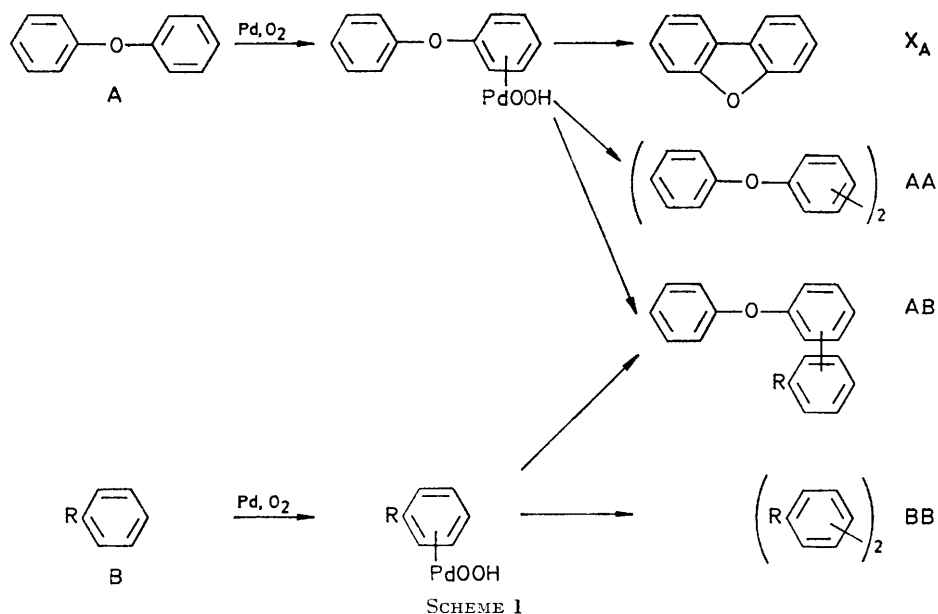
^a 4-Methoxydiphenyl ether was also studied, but the yield was considerably lower and precipitation of palladium black was observed. Similarly, anisole gave a low yield of coupling products in the palladium-catalysed reaction.⁵ ^b Yields based on palladium acetate used.

order: O > CO, CH₂ ≫ S, SO₂, NAc, NH. On the other hand, cyclisation of diphenylamine was achieved with 1 equiv. of palladium acetate in acetic acid. This indicates that electrophilic attack of a palladium(II) species is involved in the rate-determining step.¹⁰ Under our conditions, coupling reactions are catalysed by palladium(0) species which can be activated by molecular oxygen.¹¹

In the course of a study of palladium-catalysed coupling, the relative reactivity of aromatic compounds was discussed in detail from the viewpoint of a stepwise coupling process.¹² We have now performed a competitive reaction between diphenyl ether and an aromatic compound as set out in Scheme 1. For convenience of analysis, 4-nitrophenyl phenyl ether was employed because the formation of dimers of 4-nitrophenyl phenyl ether was negligible compared with that of the cyclised product. Table 3 shows that cyclisation took place considerably faster than aryl dimerisation. Competitive coupling with nitrobenzene or *p*-xylene gave a lower ratio of dimers to cyclised product (BB to X_A). With naphthalene, however, binaphthyl (BB) was formed to a much greater extent than 2-nitrodibenzofuran (X_A). These results are compatible with the report¹² that nitrobenzene and *p*-xylene gave dimers in lower yields but that the reverse was true for naphthalene. Similarly, the relative reactivity of nitration increases in the

¹¹ M. Kashima, H. Yoshimoto, and H. Itatani, *J. Catalysis*, 1973, **29**, 92.

¹² H. Yoshimoto and H. Itatani, *J. Catalysis*, 1973, **31**, 8.



order: benzene < diphenyl ether < naphthalene,^{13a} and mercuriation with mercury diacetate takes place faster with diphenyl ether than with benzene.^{13b} It is also known that the intramolecular process is faster than the

¹³ C. H. Bamford and C. F. H. Tipper, 'Comprehensive Chemical Kinetics,' vol. 13, Elsevier, New York, 1972, (a) p. 39; (b) p. 192.

intermolecular one in the cyclization of aryl-substituted halides,^{14a} and that the yields of products of intermolecular coupling are usually low in the Scholl reaction.^{14b}

Isotope Effect on the Intramolecular Ring Closure.—In

¹⁴ G. A. Olah, 'Friedel-Crafts and Related Reactions,' vol. 2, part 2, Interscience, New York, 1964, (a) ch. 22; (b) ch. 23.

the earlier work,² a primary isotope effect was observed in the oxidative coupling of hexadeuteriobenzene with 1 equiv. of palladium acetate in acetic acid, and explained in terms of disproportionation of the σ -aryl-palladium(II) complex to a biaryl and a palladium(I)

TABLE 3

Competitive reaction between 4-nitrophenyl phenyl ether and aromatic compounds (conditions as for Table 2, but ethylene glycol diacetate excluded)

B	Products (%) ^a			Ratios of	
	X _A	B-B	A-B	BB : X _A	AB : X _A
PhNO ₂	3 230	120	280	0.037	0.087
PhH	4 170	520	1 170 ^b	0.13	0.28
Naphthalene	640	1 830	540	2.8	0.84
<i>p</i> -Xylene	4 880	110	370	0.023	0.076

^a Yields based on palladium acetate used. ^b The products isolated by g.l.c. showed the molecular ion (m/e 291) in the mass spectrum.

species. However, the competitive reactions of benzene and other aromatic nuclei were not satisfactorily explained by this hypothesis. It has been proposed^{3,11} that palladiation occurs to form an aryl-Pd(II) inter-

ation of 2,8- and 2,7-dimethyldibenzofurans in air with cobalt and manganese catalysts gave, in good yields, the 2,8- and 2,7-dicarboxylic acids, respectively, characterised as their dimethyl esters. The 2,7-dicarboxylic acid may be of use in polyesters and polyamides (*cf.* ref. 16). A convenient method for the recovery and regeneration of palladium acetate is described in the Experimental section.

EXPERIMENTAL

General procedures have been described.⁵ Diphenyl ether and benzophenone were commercially available. Di-*p*-tolyl ether,¹⁷ *m*-tolyl *p*-tolyl ether,¹⁷ *o*-tolyl *p*-tolyl ether,¹⁷ *o*-isopropylidiphenyl ether¹⁷ (b.p. 144–145 °C at 10 mmHg), and 4-nitrophenyl phenyl ether¹⁸ were prepared as previously described. 4,4'-Dimethylbenzophenone was prepared by a Friedel-Crafts reaction.¹⁹ ¹³C N.m.r. spectra were obtained with a JEOL JNM PFT-100 Fourier transform spectrometer operating at 25.15 MHz, equipped with an EC-100 12K computer [spectral width 250 p.p.m. 8 191 data points for 1 000–2 000 accumulations; pulse width was 11 μ s (45°)]. The spectra were recorded for *ca.* 25% solutions in deuteriochloroform, with tetramethylsilane as internal standard.

TABLE 4

Carbon-13 chemical shifts of dibenzofuran derivatives (2) (calc. values in parentheses)

Compd.	Carbon atom												R ¹	R ²
	1	2	3	4	4a	9b	9	8	7	6	5a	9a		
(2a)	120.4 ^a	122.5 ^a	126.9 ^a	111.5 ^a	156.0	124.1	120.4 ^a	122.5 ^a	126.9 ^a	111.5 ^a	156.0	124.1		
(2b)	120.4 ^a	131.8	127.9 ^a	111.0 ^a	154.8	124.2	120.4 ^a	131.8	127.9 ^a	111.0 ^a	154.8	124.2	21.2 ^b	21.2 ^b
	(121.0)	(131.6)	(127.5)	(111.3)	(152.9)	(123.9)	(121.0)	(131.6)	(127.5)	(111.3)	(152.9)	(123.9)		
(2c)	120.3 ^a	131.9	127.5 ^a	111.0 ^a	154.5	124.3	120.0 ^a	123.7 ^a	137.3	111.9 ^a	156.9	121.6	21.9 ^b	21.3 ^b
	(121.0)	(131.6)	(127.5)	(111.3)	(152.9)	(123.9)	(120.2)	(123.1)	(136.0)	(112.1)	(155.8)	(121.0)		

^a Doublet in the off-resonance spectrum. ^b Quartet in the off-resonance spectrum.

mediate which adds to the other aryl compound. A coupling reaction with a catalytic quantity of palladium acetate showed a reasonable isotope effect in the system benzene-hexadeuteriobenzene due to hydrogen abstraction.¹¹ The isomer distributions in the systems containing toluene or *p*-xylene were reported to be 2.4 : 1 and 2.2 : 1, respectively (Scheme 2).

The competitive reaction of diphenyl ether and penta-deuteriophenyl phenyl ether afforded dibenzofurans in the ratio (determined by mass spectrometry) 2.0 : 1 (Scheme 3). The similarity between the values of isotope effects for inter- and intra-molecular coupling suggests that the reactions proceed through similar intermediates, *i.e.* aryl-palladium complexes.

Carbon-13 Chemical Shifts in Dibenzofuran Derivatives.—The dimethyldibenzofuran derivatives obtained were identified by ¹H n.m.r. spectroscopy (see Experimental section). ¹³C N.m.r. measurements were also made (Table 4). Calculations of chemical shifts by use of methyl shielding values for toluene¹⁵ are in excellent agreement with observation.

Preparation of Dibenzofurandicarboxylic Acids.—Oxid-

¹⁵ J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972, p. 94.

¹⁶ E. I. du Pont de Nemours and Co., U.S.P. 3,190,853/1965.

¹⁷ R. G. R. Bacon and O. J. Stewart, *J. Chem. Soc.*, 1965, 4953.

¹⁸ R. Q. Brewster and T. Groening, *Org. Synth.*, Coll. vol. 2, 1948, p. 446.

¹⁹ L. Gattermann, 'Die Praxis des Organischen Chemikers,' de Gruyter, Berlin, 1961, p. 296.

²⁰ (a) Y. Sugii and H. Shindo, *J. Pharm. Soc. Japan*, 1933, 53, 97; (b) R. Gerdill and E. A. C. Lucken, *J. Amer. Chem. Soc.*, 1965, 87, 213.

2.45 (s, 2 CH₃), 7.12 (H-3 and -7), 7.36 (H-4 and -6), and 7.60 (H-1 and -9) ($J_{1,3} = J_{7,9} = 1.5$, $J_{3,4} = J_{6,7} = 7.5$, $J_{1,4} = J_{6,9} = 0.6$ Hz); M^+ 196 (Found: C, 85.35; H, 6.25. Calc. for C₁₄H₁₂O: C, 85.7; H, 6.15%). The oily fraction of b.p. 125–150 °C at 0.5 mmHg was chromatographed on alumina [hexane–benzene (1:1)] to give the dimers, which were shown to consist of three isomers by g.l.c.; M^+ 394 (Found: C, 84.95; H, 6.35. Calc. for C₂₈H₂₄O₂: C, 85.25; H, 6.65%).

Coupling of *m*-Tolyl *p*-Tolyl Ether.—Treatment similar to the above gave 2,7-dimethyldibenzofuran (2c) (13.83 mmol) and dimers (0.89 mmol). Fractional distillation gave material boiling at 125–130 °C and 2 mmHg (2.3 g). Two recrystallisations from ethanol gave pure (2c) (1.6 g), m.p. 82–83 °C; δ (CCl₄) 2.47 (s, 2 CH₃), 7.02 (H-8), 7.10 (H-3), 7.28 (H-6), 7.35 (H-4), 7.60 (H-1), and 7.67 (H-9) ($J_{1,3} = 1.5$, $J_{3,4} = 7.5$, $J_{1,4}$ ca. 0.6, $J_{6,8} = 1.2$, $J_{3,9} = 7.5$, $J_{6,9}$ ca. 0.5 Hz); M^+ 196 (Found: C, 85.55; H, 6.25%). The oily fraction of b.p. 140–160 °C at 0.5 mmHg showed M^+ 394 (dimers).

Coupling of 4-Nitrophenyl Phenyl Ether.—Similar treatment gave 2-nitrodibenzofuran (7.84 mmol), isolated as yellow needles (1.1 g), m.p. 150–151 °C (from ethanol) (lit.,²¹ 150.5–151.5 °C); M^+ 213 (Found: C, 67.55; H, 3.25; N, 6.6. Calc. for C₁₂H₇NO₃: C, 67.6; H, 3.3; N, 6.55%). A trace of dimerised product was detected by liquid chromatography, but not by g.l.c.

Similarly, *o*-tolyl *p*-tolyl ether, *o*-isopropylphenyl phenyl ether, benzophenone, and 4,4'-dimethylbenzophenone, gave 2,6-dimethyldibenzofuran, 4-isopropylidibenzofuran, fluorenone, and 3,6-dimethylfluorenone, respectively, identified by g.l.c.–mass spectrometry.

Competitive Reaction of Diphenyl Ether and its Homologues (Table 2).—A mixture of diphenyl ether (A) (35 mmol), its homologue (B) (35 mmol), palladium acetate (0.15 mmol), acetylacetone (0.15 mmol), and ethylene glycol diacetate (5 ml) was shaken at 150 °C for 5 h (initial O₂–N₂ pressure 50 kg cm⁻²). Yields of cyclised products were determined by g.l.c.

Competitive Reactions with 4-Nitrophenyl Phenyl Ether (Table 3).—Yields were determined by g.l.c.

Synthesis of Pentadeuteriophenyl Phenyl Ether and its Competitive Reaction with Diphenyl Ether.—Hexadeuteriobenzene (50 g; Merck, 99% ²H₆) was brominated²² with bromine (96 g, ca. 31 ml) in the presence of reduced iron powder (2 g) to give bromopentadeuteriobenzene (73 g, 76%) and 1,4-dibromotetradeteriobenzene (7.2 g). A mixture of potassium phenoxide [prepared¹⁷ from phenol (47 g) and potassium hydroxide (28 g)], bromopentadeuteriobenzene (32.4 g), dimethylacetamide (20 ml), and copper powder (0.5 g) was stirred under nitrogen at 210–220 °C for 4 h. The mixture was then poured into ice–water (300 ml) containing sodium hydroxide (10 g) and stirred to remove the excess of phenol. The ethereal extract was washed with dilute sodium hydroxide solution and dried (Na₂SO₄). Distillation gave pentadeuteriophenyl phenyl ether, b.p. 97–98 °C at 3 mmHg (lit.,²³ 97.5–98.5 °C at 3 mmHg for Ph₂O) (92% ²H₅).

A mixture of pentadeuteriophenyl phenyl ether (35 mmol), diphenyl ether (35 mmol), palladium acetate (0.15 mmol), acetylacetone (0.15 mmol), and ethylene glycol

diacetate (5 ml) was shaken at 150 °C for 5 h under an initial O₂–N₂ pressure of 50 kg cm⁻². G.l.c. analysis showed the presence of dibenzofuran (9.62 mmol). The isomer composition of deuterium-containing products, which were separated by g.l.c., was determined by mass spectrometry (Hitachi RMU-6 instrument operating at 15 eV; no fragmentation ion was observed). The peak ratios were calculated from the average of three scans. The ratio of dibenzofuran to tetradeteriodibenzofuran was obtained after correction for H–D exchange during the reaction.

Oxidation of 2,8-Dimethyldibenzofuran.—A mixture of the dibenzofuran (2b) (0.90 g), cobalt diacetate tetrahydrate (0.050 g), manganese diacetate tetrahydrate (0.050 g), ammonium bromide (0.050 g), and acetic acid (10 ml) was shaken at 180 °C for 2 h (initial pressure 65 kg cm⁻² of 1:1 oxygen–nitrogen). Dibenzofuran-2,8-dicarboxylic acid formed was filtered off and washed with acetic acid, water, and methanol; yield 1.11 g (94%); m.p. >360 °C; ν_{\max} (KBr) 1 670s cm⁻¹ (CO). The acid (0.25 g), thionyl chloride (4 ml), and several drops of pyridine (as a catalyst) were refluxed for 2 h. The excess of thionyl chloride was distilled off, and the resulting acid chloride was refluxed for 2 h with methanol (10 ml) and pyridine (0.5 ml). The product was filtered off and washed with cold methanol, giving a powder (0.16 g), which was recrystallised from toluene–*n*-hexane to afford dimethyl dibenzofuran-2,8-dicarboxylate, m.p. 164–166 °C (lit.,¹⁶ 167 °C); ν_{\max} (KBr) 1 710s (CO) and 1 250s cm⁻¹ (CO); δ (CDCl₃) 3.97 (s, 2 CH₃), 7.54 (H-4 and -6), 8.17 (H-3 and -7), and 8.65 (H-1 and -9) ($J_{1,3} = J_{7,9} = 1.5$, $J_{3,4} = J_{6,7} = 7.8$, $J_{1,4} = J_{6,9} = 0.6$ Hz); M^+ 284 (Found: C, 67.55; H, 4.4. Calc. for C₁₆H₁₂O₅: C, 67.6; H, 4.25%).

Oxidation of 2,7-Dimethyldibenzofuran (H. YOSHIMOTO).—The dibenzofuran (1.00 g) was treated as described above, giving dibenzofuran-2,7-dicarboxylic acid (1.21 g, 93%); m.p. >360 °C; ν_{\max} (KBr) 1 670s cm⁻¹ (CO). The acid (1.00 g) was shaken in an autoclave with methanol (20 ml) and toluene–*p*-sulphonic acid (0.10 g) at 150 °C for 4 h. The product was filtered off and washed with methanol, giving a powder (0.91 g), which was recrystallised from ethyl acetate–*n*-hexane to afford the dimethyl ester, m.p. 152–153 °C; ν_{\max} (KBr) 1 710s (CO) and 1 245s cm⁻¹ (CO); δ (CDCl₃) 3.96 (s, 2 CH₃), 7.53 (H-4), 7.98 (H-6), 8.06 (H-9), 8.07 (H-8), 8.16 (H-3), and 8.60 (H-1) ($J_{1,3} = 1.5$, $J_{3,4} = 7.8$, $J_{1,4} = 0.6$, $J_{6,8}$ ca. 1.2, $J_{8,9}$ ca. 10, $J_{6,9}$ ca. 0.6 Hz); M^+ 284 (Found: C, 67.7; H, 4.1%).

Recovery and Regeneration of Palladium Catalyst.—A large-scale experiment with palladium acetate (3.36 g, 15.0 mmol) was carried out in a 5 l autoclave. After reaction, the autoclave was cooled, degassed, and refilled to a pressure of 30 kg cm⁻² with hydrogen. After agitation at 60 °C for 2 h, the precipitated palladium black was collected and washed with acetone (yield 1.572 g, 98.6%).

(a) Palladium black (1.064 g, 10 mmol) and glacial acetic acid (25 ml) were shaken in an autoclave at 60 °C for 1 h under hydrogen (40 kg cm⁻²). The contents were transferred to a 100 ml flask and refluxed for 1 h with concentrated nitric acid (0.5 ml).²⁴ Unchanged palladium (0.08 g) was collected by filtration of the hot solution. Cooling gave palladium acetate (1.618 g, 73%), which was

²¹ M. J. S. Dewar and D. S. Urch, *J. Chem. Soc.*, 1957, 345.

²² H. Erlenmeyer, H. Lobeck, and A. Epprecht, *Helv. Chim. Acta*, 1936, 19, 793.

²³ Beilsteins 'Handbuch der Organischen Chemie,' 1965, EIII 6, 562.

²⁴ T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.

filtered off. The mother liquor, containing more palladium acetate, could be used in the following regeneration procedure.

(b) A mixture of palladium black (1.064 g, 10 mmol), sodium borohydride (1.13 g, 30 mmol), and ethanol (30 ml) was refluxed for 1 h. The palladium black was then filtered off and washed with water and glacial acetic acid.

Refluxing with glacial acetic acid (25 ml) and concentrated nitric acid (0.5 ml) for 1 h gave palladium acetate (1.558 g, 76%) and unchanged palladium (0.096 g). The mother liquor contained the remaining palladium acetate.

Without pre-treatment of palladium black with hydrogen or sodium borohydride, palladium acetate was not obtained.

[5/1938 Received, 6th October, 1975]
