77. *The Synthesis of Methyl- and Dimethyl-dibenzofurans.*

By S. Trippett.

The methyl- and the dimethyl-dibenzofurans having both methyl groups in the same ring have been synthesised and their spectra recorded.

Degradative work on rhodomyrtoxin, the toxic principle of the immature Australian finger cherry (*Rhodomyrtus macrocarpa* Benth.), gave a compound which was probably a dimethyldibenzofuran having both methyl groups in the same ring.[1] In order to identify this, the six possible dimethyldibenzofurans and the four methyldibenzofurans have been synthesised, and their ultraviolet and infrared spectra recorded.

The general method adopted was essentially that of Ebel.[2] 2-Bromo*cyclo*hexanone

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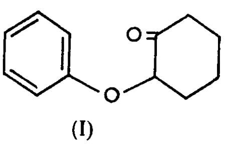
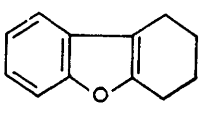
[1] Trippett, preceding paper.

[2] Ebel, *Helv. Chim. Acta*, 1929, **12**, 3.

with a sodium phenoxide gave a keto-ether (I) which, on treatment with concentrated sulphuric acid or polyphosphoric acid, cyclised to a 1 : 2 : 3 : 4-tetrahydrodibenzofuran (II). This, upon dehydrogenation with palladium–charcoal at 230°, gave a dibenzofuran (III) in good yield.



(I)



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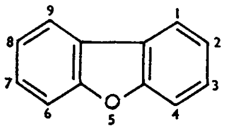

(III)

The synthesis of 2- and 4-methyldibenzofuran and of 1 : 3-, 2 : 3-, 3 : 4-, 1 : 4-, and 2 : 4-dimethyldibenzofuran by this method was straightforward and unambiguous. However, 2-*m*-tolyloxy*cyclo*hexanone cyclised to a mixture of the possible products which could not be separated, while 2-(3 : 4-dimethylphenoxy)*cyclo*hexanone cyclised entirely on the 2′-position. For the synthesis of 1- and 3-methyldibenzofuran, and of 1 : 2-dimethyldibenzofuran, the methyl groups were therefore introduced in the *cyclo*hexanone part of the molecule.

The 2-bromo-6-methyl*cyclo*hexanone required for the synthesis of 1-methyldibenzofuran was obtained by bromination of 3-methyl-2-oxo*cyclo*hexanecarboxylic acid, followed by decarboxylation. The keto-ether from condensation with sodium phenoxide, and the resulting 1-methyldibenzofuran, could not be obtained analytically pure, but its structure was confirmed by a comparison of its spectra with those of the mixture of 1- and 3-methyldibenzofuran resulting from 2-*m*-tolyloxy*cyclo*hexanone. *N*-Bromosuccinimide and 2-methyl*cyclo*hexanone are reported[3] to give 2-bromo-2-methyl*cyclo*hexanone, and this has been confirmed. However, *N*-bromosuccinimide and 2 : 3-dimethyl*cyclo*hexanone gave a bromo-ketone which coupled with sodium phenoxide to give a crystalline keto-ether in good yield. This is formulated as 5 : 6-dimethyl-2-phenoxy*cyclo*hexanone because of the absence in its infrared spectrum of any band in the 6·9—7·15 μ region. Such a band has been found to be characteristic of a methylene group adjacent to carbonyl in a six-membered ring (see Table 1). Cyclisation with polyphosphoric acid gave only a poor yield of the desired compound, dehydrogenation of which gave 1 : 2-dimethyldibenzofuran.

TABLE 1. *Infrared spectra of substituted* cyclo*hexanones in the region* 6·9—7·15μ.

Subst.	Absorption (μ)	Subst.	Absorption (μ)	Subst.	Absorption (μ)
—	6·99 (s)	2-Bromo-2-methyl ...	7·01 (m)	2-(2 : 3-Dimethyl-phenoxy)	6·97 (w)
2-Methyl	6·98 (m)	2-Ethoxycarbonyl ...	7·01 (m)	2 : 6-Dimethyl	—
4-Methyl	7·01 (s)	2-(3 : 4-Dimethyl-phenoxy)	6·97 (w)	2-Ethoxycarbonyl-6-methyl	—
2 : 3-Dimethyl	6·98 (m)				

TABLE 2. *Spectra of substituted dibenzofurans.*

Subst.	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$	$\lambda_{max.}$ (μ)	Subst.	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$	$\nu_{max.}$ (μ)
—	249, 280	17·4, 14·2	8·38 (s)	1 : 3-Dimethyl	255, 283	19·8, 20·6	8·38 (m)
1-Methyl	253, 280	—	8·40 (m)	1 : 4-Dimethyl	255·5, 280	15·8, 18·1	8·22 (s)
2-Methyl	251, 285	20·1, 18·0	8·35 (s)	2 : 3-Dimethyl	252, 289	19·2, 17·7	8·26 (s)
3-Methyl	251·5, 285	20·1, 18·3	8·24 (s)	2 : 4-Dimethyl	253, 285	15·9, 14·9	8·41 (s)
4-Methyl	252, 281	15·7, 12·4	8·4 (s)	3 : 4-Dimethyl	253·5, 284, 288	19·5, 17·9, 18·5	8·36 (s)
1 : 2-Dimethyl	254, 284	12·8, 10·3	8·38 (s)				

The ultraviolet and infrared spectra of the methyl- and dimethyl-dibenzofurans are given in Table 2. In general, the infrared spectra are dominated by a sharp strong band in the 8·3—8·4 μ region which can be used for the identification of alkyldibenzofurans.

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[3] Rinne, Deutsch, Bowman, and Jaffe, *J. Amer. Chem. Soc.*, 1950, **72**, 5759.

EXPERIMENTAL

The methods used are illustrated by the synthesis of 1 : 3-dimethyldibenzofuran.

*2-Bromo*cyclo*hexanone.*—*cyclo*Hexanone (15 g.), *N*-bromosuccinimide (26·7 g.), and carbon tetrachloride (200 ml.) were heated on the steam-bath under reflux for 30 min., then filtered, the solvent was removed under reduced pressure, and the residue distilled to give 2-bromo*cyclo*hexanone (18 g.), b. p. 61°/0·01 mm. The reaction was violent and could not conveniently be carried out on a larger scale.

*2-(3 : 5-Dimethylphenoxy)*cyclo*hexanone.*—2-Bromo*cyclo*hexanone (18 g.) and sodium 3 : 5-dimethylphenoxide (from 14·2 g. of 3 : 5-xylenol) were shaken overnight at room temperature in benzene (200 ml.), the suspension washed with water, dilute alkali, and water, and dried, and the solvent removed. Crystallisation of the residue from light petroleum gave 2-(3 : *5-dimethylphenoxy)*cyclo*hexanone* (16 g.), m. p. 82—84°.

In this way the tabulated *2-phenoxy*cyclo*hexanones* were prepared.

*2-Phenoxy*cyclo*hexanones.*

		Found (%)		Required (%)	
Subst.	M. p.	C	H	C	H
2′-Me ...	65—66°	76·1	7·7	76·4	7·9
3′-Me ...	72—74	76·3	7·8		
4′-Me ...	91—93	76·2	7·6		
4-Me	117—119	76·5	7·4		

		Found (%)		Required (%)	
Subst.	M. p.	C	H	C	H
2′ : 3′-Me$_2$	75—77°	77·1	8·1	77·0	8·3
2′ : 5′-Me$_2$	(b. p. 120°/ 0·55 mm.)	77·1	8·2		
2′ : 4′-Me$_2$	91—92	77·1	8·2		
3′ : 4′-Me$_2$	66—67	77·0	8·1		
3′ : 5′-Me$_2$	82—85	77·4	8·2		
5 : 6-Me$_2$	124—126	77·3	8·2		

1 : 2-3 : 4-Tetrahydro-6 : 8-dimethyldibenzofuran.—The above keto-ether (2 g.) was shaken at 100° for 3 hr. with phosphoric acid (20 ml.; *d* 1·74) and phosphoric oxide (10 g.), the suspension poured into water, and the solid filtered, washed, and dried. Crystallisation of the solid from light petroleum at 0° gave 1 : 2 : 3 : *4-tetrahydro-6* : *8-dimethyldibenzofuran* (1·7 g.), m. p. 65—66°.

In this way the annexed 1 : 2 : 3 : *4-tetrahydrodibenzofurans* were prepared.

1 : 2 : 3 : *4-Tetrahydrodibenzofurans.*

	M. p. or	Found (%)		Required (%)	
Subst.	b. p.	C	H	C	H
3-Me	45—47°	83·8	7·6	83·8	7·6
6-Me	100°/ 0·2 mm.	84·0	7·7		
8-Me	100°/ 0·2 mm.	84·4	7·7		

	M. p. or	Found (%)		Required (%)	
Subst.	b. p.	C	H	C	H
6 : 7-Me$_2$	50—51°	83·6	7·9	84·0	8·0
6 : 8-Me$_2$	10	83·7	7·8		
6 : 9-Me$_2$	24—26	83·9	7·8		
7 : 8-Me$_2$	83—84	83·7	7·9		
7 : 9-Me$_2$	65—66	84·0	8·0		

1 : 3-Dimethyldibenzofuran.—The above tetrahydro-compound (1 g.) was heated under nitrogen at 230° for 5 hr. with 5% palladium–charcoal (0·5 g.). Extraction of the residue with light petroleum, removal of solvent, and crystallisation from ethanol gave 1 : *3-dimethyldibenzofuran* (0·7 g.), m. p. 45°.

In this way the tabulated *dibenzofurans* were prepared.

Dibenzofurans.

	M. p. or	Found (%)		Required (%)	
Subst.	b. p.	C	H	C	H
1-Me	105°/ 0·2 mm.	—	—	85·7	5·5
2-Me[4] ...	45—45·5	85·7	5·5		
3-Me[5] ...	61—62	85·9	5·5		
4-Me[6] ...	105°/ 0·2 mm.	85·4	6·0		

	M. p. or	Found (%)		Required (%)	
Subst.	b. p.	C	H	C	H
1 : 2-Me$_2$	115°/ 0·2 mm.	85·3	6·7	85·7	6·2
1 : 3-Me$_2$	45—45·5	85·6	6·0		
1 : 4-Me$_2$	17—18	86·0	6·2		
2 : 3-Me$_2$	92	85·7	6·0		
2 : 4-Me$_2$	120°/ 0·2 mm.	85·6	6·4		
3 : 4-Me$_2$	55—56	85·4	5·9		

THE UNIVERSITY, LEEDS, 2.

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[4] Mayer and Krieger, *Ber.*, 1922, **55**, 1662.

[5] Suggii and Shindo, *J. Pharm. Soc. Japan*, 1934, **54**, 149.

[6] Kruber, *Ber.*, 1932, **65**, 1382.