

A Short Synthesis of Dibenzofurans and Dibenzothiophenes

Michael Black,^a J. I. G. Cadogan,^{*b} and Hamish McNab^{*a}

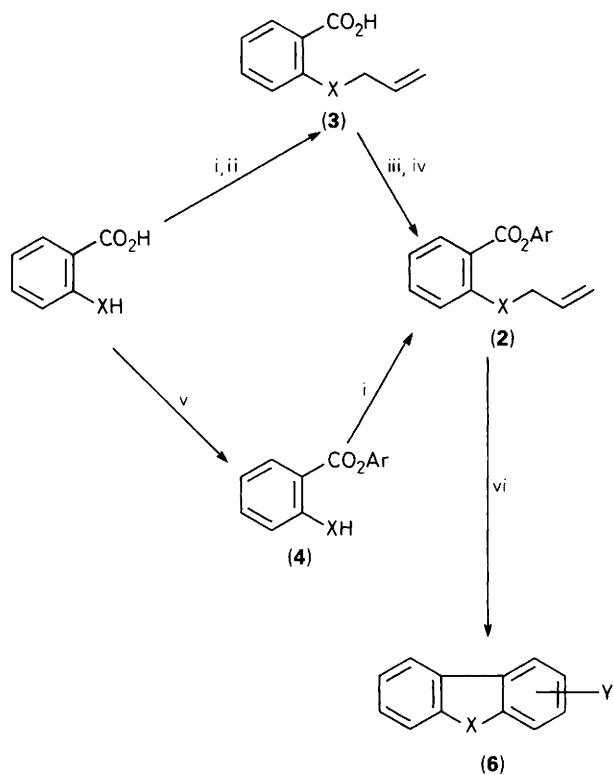
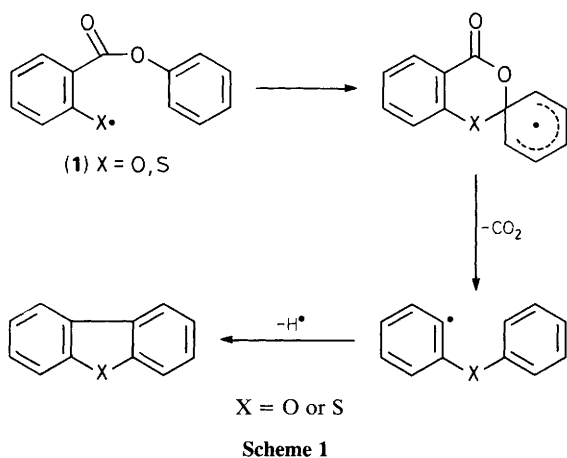
^a Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

^b BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, U.K.

An efficient synthesis of dibenzofurans and dibenzothiophenes from aryl salicylates is described, which involves a novel rearrangement–extrusion–cyclisation sequence of *o*-substituted phenoxy and thiophenoxy radicals.

Traditional ways of synthesising dibenzofurans and dibenzothiophenes, including solution free radical methods, suffer from the disadvantages of low yields and/or inaccessibility of starting materials.^{1,2} We have developed a simple preparative route based on gas phase free radical methodology³ applicable

to either ring system, using salicylates and phenols as readily available starting materials. The key step (Scheme 1) involves a novel rearrangement–extrusion–cyclisation sequence of the *o*-substituted phenoxy and thiophenoxy radicals (**1**) to create the new five-membered ring.



Scheme 2. Reagents and conditions: i, $\text{H}_2\text{C}=\text{C}(\text{H})\text{CH}_2\text{Br}$, K_2CO_3 , dimethylformamide; ii, NaOH ; iii, SOCl_2 ; iv, ArOH , 4-dimethylaminopyridine; v, POCl_3 , ArOH ; vi, flash vacuum pyrolysis (650°C , 10^{-3} Torr).

The ready availability of the radical precursors (2) via (3) or (4)⁴ is an attractive feature of the overall method.[†] However, the route via (4) is inappropriate for electron-withdrawing Ar groups, because of competing Smiles rearrangement in the subsequent alkylation, whereas the route via (3) fails for the *S*-allyl compound due to base-induced rearrangement⁵ to the *S*-propenyl derivative (5) at the ester hydrolysis stage [step (ii)].

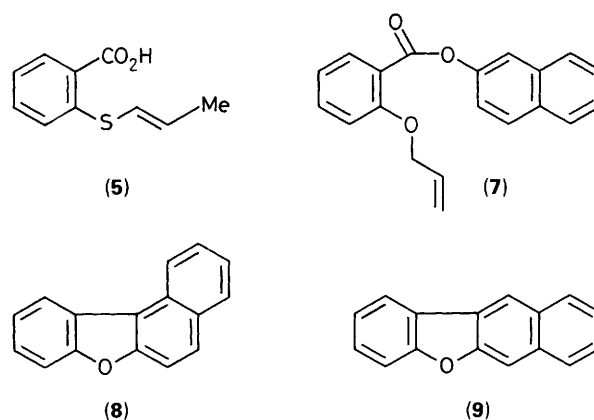
The conditions for the pyrolysis (650°C , 10^{-3} Torr) are compatible with the presence and electronic nature of a wide range of substituents (Table 1). Yields of dibenzofuran or dibenzothiophene derivatives (6) are generally high, particu-

[†] All new compounds were characterised by their spectra and by elemental analyses.

Table 1.

Precursor (2)		Yield of (6)/ %
X	Y	
O	H	62
	<i>p</i> -Me	70
	<i>p</i> -Cl	87
	<i>p</i> -NO ₂	90
	<i>p</i> -CN	73
	<i>p</i> -OMe	80
	<i>m</i> -Me	59 ^{a,b}
S	H	88
	<i>p</i> -Me	70
	<i>p</i> -Cl	94
	<i>m</i> -Me	58 ^a
	<i>o</i> -Me	39

^a 1:1 mixture of 1- and 3-substituted products. ^b The overall yield estimated from ¹H NMR.



larly for *p*-substituted Ar groups, which give a single product isomer. The only significant side product is a trace of the phenol (ArOH), which can be removed readily by base extraction. Although *m*-methyl groups in Ar yield a statistical mixture of 1- and 3-substituted products, some selectivity has been observed in more complex cases. For example the β -naphthyl compound (7) gives a 4:1 ratio of γ : β brazan [(8) and (9), respectively] in 91% overall yield on pyrolysis at 650°C : intermolecular radical attack at the α - and β -positions of naphthalene gives similar regioselectivity.⁶

Gas-phase radical cyclisations on *o*-substituted aryl rings may be subject to complicating factors,³ but nevertheless 4-methyldibenzofuran and 4-methyldibenzothiophene could be isolated in 31 and 39% yields respectively.

Further studies of the mechanism of the pyrolysis step, and application to more complex systems are under investigation.

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