A Short Synthesis of Dibenzofurans and Dibenzothiophenes

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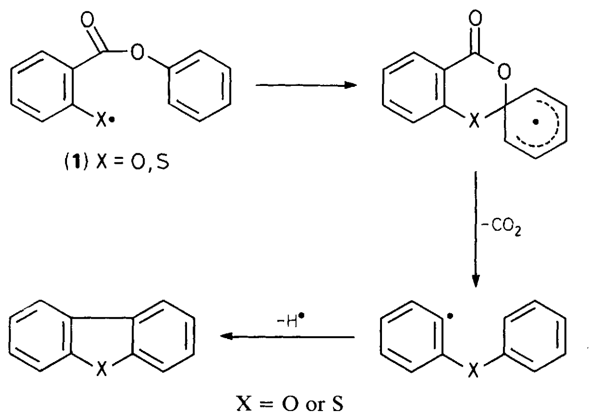
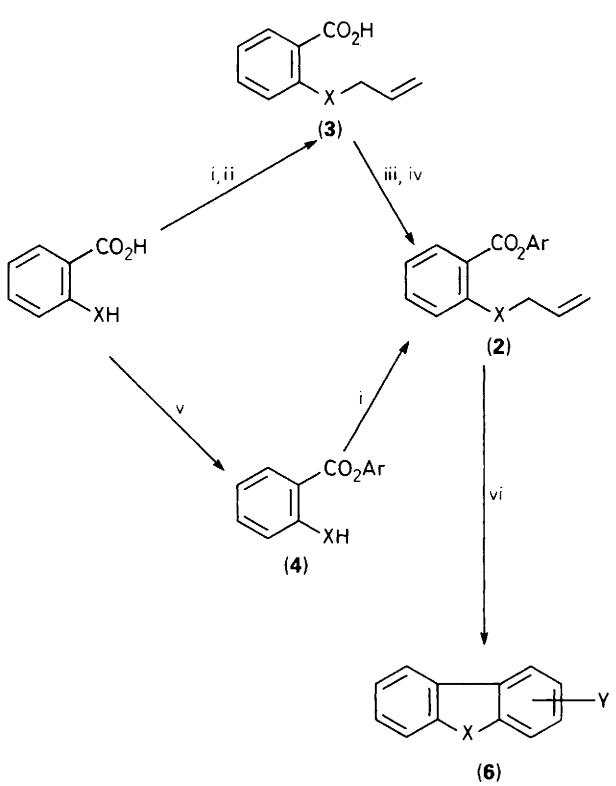
An efficient synthesis of dibenzofurans and dibenzothiophenes from aryl salicylates is described, which involves a novel rearrangement–extrusion–cyclisation sequence of *o*-substituted phenoxyl and thiophenoxyl radicals.

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 methodology[3] 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 phenoxyl and thiophenoxyl radicals (**1**) to create the new five-membered ring.



Scheme 1



Scheme 2. *Reagents and conditions:* i, $H_2C=C(H)CH_2Br$, 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).

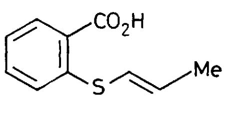
The ready availability of the radical precursors (**2**) *via* (**3**) or (**4**)[4] is an attractive feature of the overall method.† However, the route *via* (**4**) is inappropriate for electron-withdrawing Ar groups, because of competing Smiles rearrangement in the subsequent alkylation, whereas the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

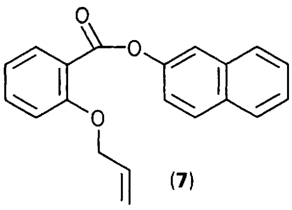
Table 1.

Precursor (2)		Yield of (6)/
X	Y	%
O	H	62
	p-Me	70
	p-Cl	87
	p-NO_2	90
	p-CN	73
	p-OMe	80
	m-Me	59[a,b]
	o-Me	31
S	H	88
	p-Me	70
	p-Cl	94
	m-Me	58[a]
	o-Me	39

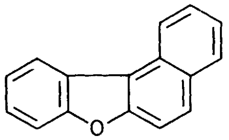
[a] 1 : 1 mixture of 1- and 3-substituted products. [b] The overall yield estimated from ^1H NMR.



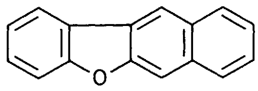
(5)



(7)



(8)



(9)

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