New Gas Phase Reactions of Substituted Benzyl, Phenylaminyl, and Phenoxyl Radicals. Rearrangements to Fused 5- and 6-Membered Heterocyclic Systems

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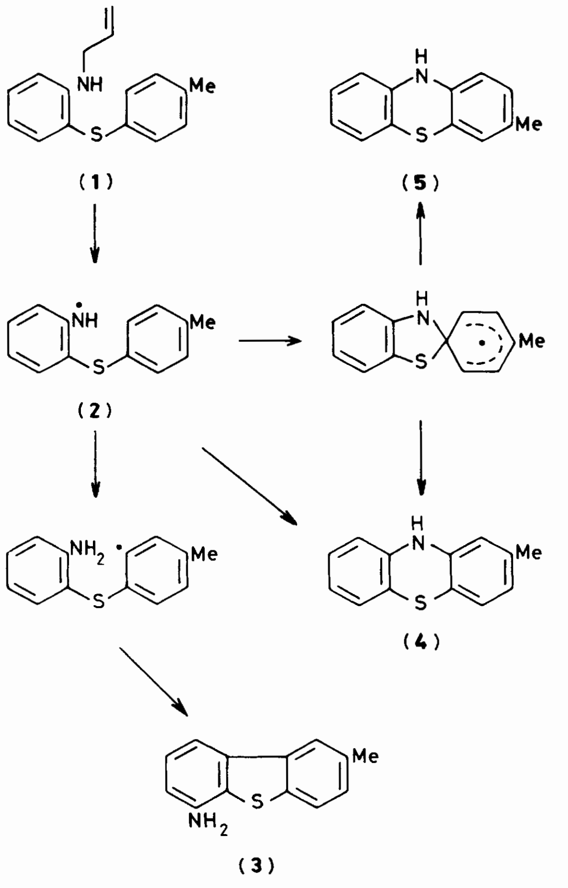
Flash vacuum pyrolysis studies of substituted benzyl, phenylaminyl, and phenoxyl radicals have revealed three new classes of reactions: formation of five-membered ring products *via* intramolecular abstraction of an aromatic hydrogen atom, formation of six-membered rings *via* spirodienyl radical intermediates, and isomerisation of *o*-phenoxybenzyl into *o*-benzylphenoxyl radicals and *vice versa*.

Studies of gas phase reactions of radicals of intermediate size *e.g.* those containing more than one aromatic ring, have been rare, in contrast to those of reactions carried out in solution. In exploring this new ground we have observed several new reactions including an intramolecular abstraction of an aromatic hydrogen atom, which appears to be unprecedented in both solution and the gas phase.

Thus, generation of the aminyl radical (**2**) by flash vacuum pyrolysis (f.v.p) of the *N*-allyl precursor[1] (**1**) gave 6-amino-2-methyldibenzothiophene (**3**; 34%) and a mixture of 2- (**4**; trace) and 3-methylphenothiazine (**5**; 14%).† This suggests reaction as in Scheme 1 *via* novel internuclear hydrogen transfer followed by cyclisation to give the five-membered thiophene ring (**3**). In competition with this are cyclisation of the radical (**2**) to give 2-methylphenothiazine (**4**) and, *via* a spirodienyl radical, rearrangement to give 3-methylphenothiazine (**5**).

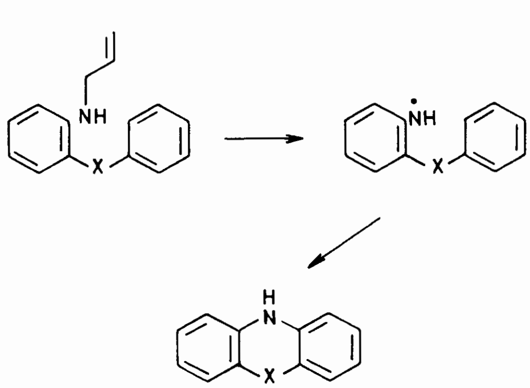


Scheme 1

Reaction of the corresponding CO and CH_2 bridged aminyl radicals proceeded only by cyclisation to give six-membered rings in high yield (Scheme 2).

Although the formation of fused six-membered heterocycles from arylnitrenes *via* rearrangement through spirodienyl type intermediates is well established,[2] the corresponding reaction of radicals is without precedent in the gas phase, and there is only one report of direct radical internuclear cyclisation; that of the formation of xanthene (**11**) in low yield from the *o*-phenoxybenzyl radical (**7**) by f.v.p.[3]

In the light of our results using allyl precursors, it was of interest to attempt the preparation of this *o*-phenoxybenzyl radical by f.v.p. of allyl *o*-benzylphenyl ether (**9**). This reaction also gave a low yield of xanthene, but the major products were 1-hydroxyfluorene (**13**) and *o*-benzylphenol (**12**). In our hands, repetition of the earlier experiments with the oxalate (**6**)[3] gave the same set of major products. The formation of (**13**) in both cases (Scheme 3) not only points to intramolecular hydrogen transfer followed by cyclisation to give a five-membered ring *i.e.* analogous to the reaction in Scheme 1, but also to interconversion of the *o*-phenoxybenzyl and *o*-benzylphenoxyl radicals *via* the spirodienyl radical (**8**). Such isomerisations have not been observed before. Xanthene can result from direct cyclisation of the radicals (**7**) and (**10**)



X = CH_2; acridan (+ acridine) 60%
X = CO; acridone 80%

Scheme 2

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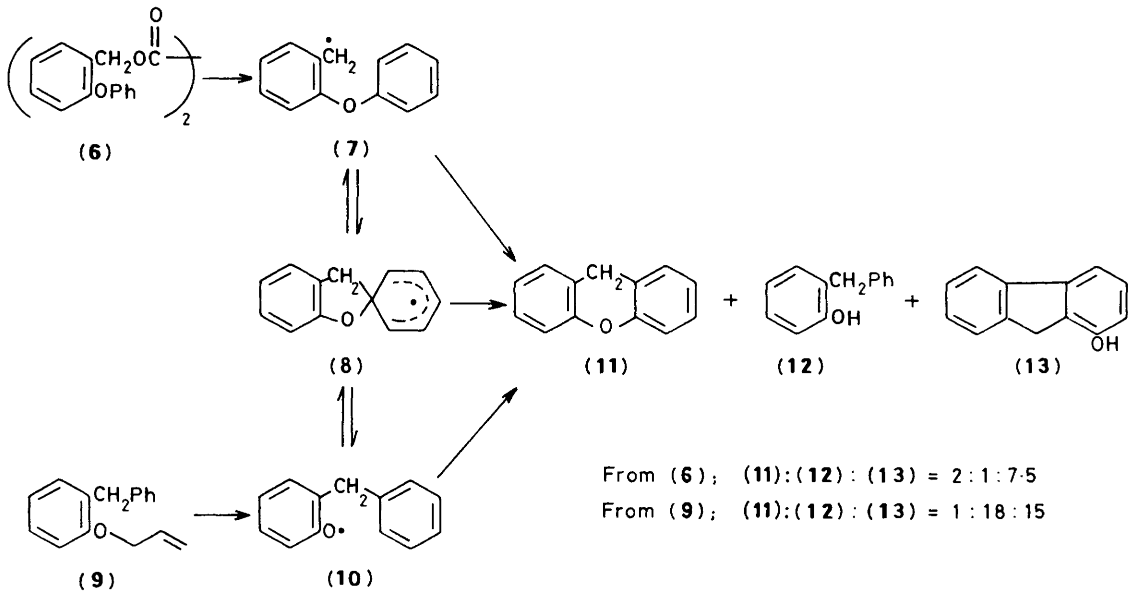
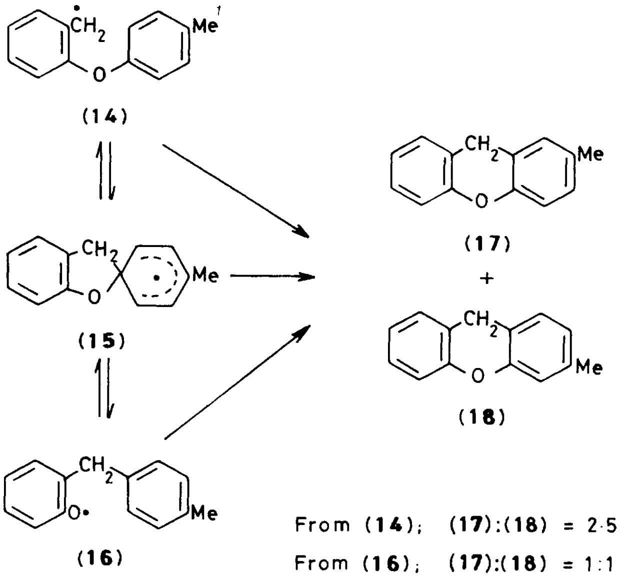
† In all cases, mixtures were separated by column chromatography on alumina: new compounds were characterised by spectra and by elemental analysis. Analysis of product ratio was made by ^1H and ^{13}C n.m.r. spectroscopy of crude pyrolysates.



From (6); (11):(12) : (13) = 2 : 1 : 7·5
From (9); (11):(12) : (13) = 1 : 18 : 15

Scheme 3

and/or *via* direct rearrangement of the spirodienyl radical. As a test of this, we examined the methylxanthene fraction from the methyl labelled radicals (**14**) and (**16**) (Scheme 4) in the expectation that direct cyclisation should lead only to xanthenes [(**17**) from (**14**)] and [(**18**) from (**16**)] while equilibration through the spirodienyl (**15**) should give the same mixture of both xanthenes in each case. In practice, mixtures were formed in each experiment, though in different ratios. We conclude, therefore, that under our conditions, equilibration is incomplete, and reaction *via* the spirodienyl (**15**) competes with direct cyclisation.



From (14); (17):(18) = 2·5 : 1
From (16); (17):(18) = 1 : 1

Scheme 4

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References

1 J. I. G. Cadogan, C. L. Hickson, and H. McNab, *J. Chem. Res.*, 1983, (S) 243, (M) 2247.
2 J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Rev.*, 1974, **3**, 87.
3 W. S. Trahanovsky and C. C. Ong, *J. Am. Chem. Soc.*, 1970, **92**, 7174.