Pyrolyses of *o*-Alkoxy- and *o*-Alkylthio-*N*-allylanilines and of Some Related *O*- and *S*-Allyl Compounds

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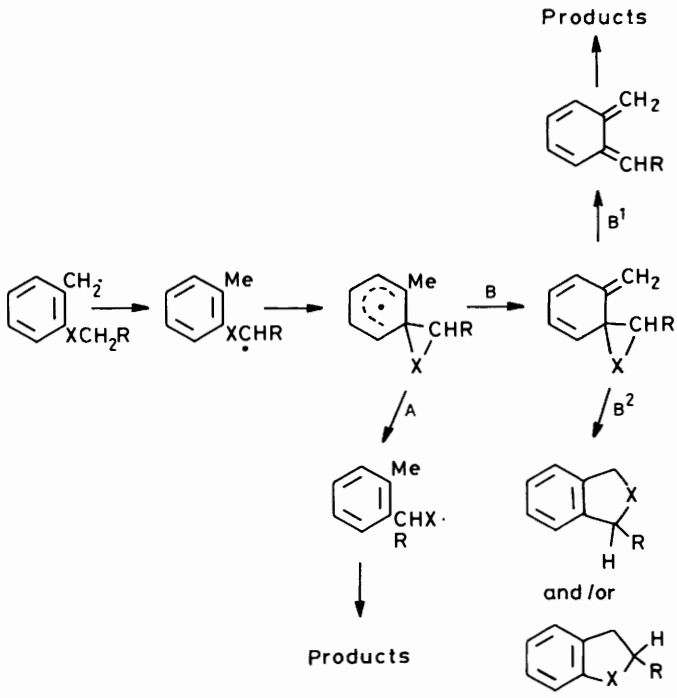
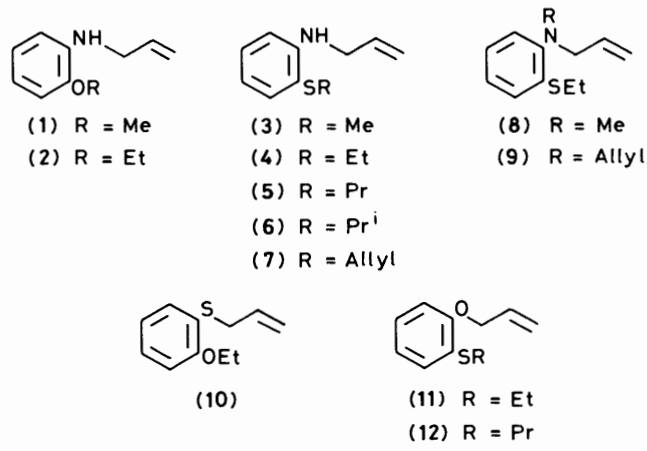
The *o*-substituted allyl compounds (**1**)—(**12**) have been pyrolysed in order to generate aminyl, phenoxyl, and thiophenoxyl radicals with adjacent substituents. In all cases, products are formed by intramolecular hydrogen transfer from the substituent to the radical centre. This process may be followed by rearrangement to give an aldehyde, by heteroatom extrusion to give an alkene, or by ring formation to give five-membered ring heterocycles (Scheme 1, routes A, B^1, and B^2 respectively). The distribution of products formed by each route is dependent both on the nature of the *o*-substituent, and on the nature of the initial radical.

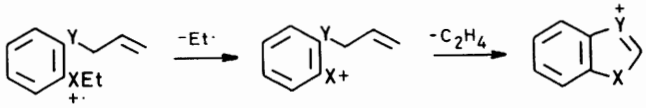
We have shown that benzyl radicals, generated by flash vacuum pyrolysis, interact with adjacent alkoxy substituents by hydrogen transfer and rearrangement to give aldehydes (Scheme 1, route A).[1,2] Thioalkoxyl substituents can also donate a hydrogen atom to adjacent benzyl radicals, but products are formed instead either by heterocyclisation and/or by sulphur extrusion (Scheme 1, route B).[1] In this paper, we report the formation and reactions of analogous anilino and phenoxyl radicals. In one previous example, *o*-hydroxybenzaldehyde was obtained from the *o*-methoxyphenoxyl radical:[3] the corresponding *O*-allyl compound was used as the radical generator, and we have similarly employed *N*-allyl compounds as efficient sources of aromatic aminyl radicals in the gas phase.[4] The allyl precursors (**1**)—(**12**) for the present study were synthesized from the parent 1,2-disubstituted benzene by specific alkylation reactions (see Experimental section). The position of alkylation was determined unambiguously by ^1H and ^{13}C n.m.r. spectroscopy.



Scheme 1.



As found for simple *N*-allyl compounds,[4] the mass spectroscopic behaviour of compounds (**1**)—(**12**) is different from the expected thermal breakdown. In general, electron-impact induced cleavage of the *O*- or *S*-alkyl group is followed by loss of C_2H_4 from the allyl substituent, with probable cyclisation (Scheme 2). An alternative mass spectroscopic cyclisation of the allyl group, which is important for the *o*-alkylthio derivatives (**3**)—(**7**) probably gives the quinolinium ion [From (**4**): Found M^+, 130.0659. C_9H_8N requires 130.0657], whereas complete loss of the allyl group is significant only for the *O*-allyl compounds (**11**) and (**12**). The *O*,*S*-substituted derivatives (**10**)—(**12**) give peaks at *m*/*z* 124 or 125, due to the *o*-quinonoid fragment (**13**) or its protonated form.



m/*z*	*m*/*z*	*m*/*z*
177(100)	148(95)	120(53)
193(100)	164(92)	136(89)[a]
194(100)	165(17)	137(34)
194(81)	165(50)	

(**2**) X = O, Y = NH; (**4**) X = S, Y = NH; (**10**) X = O, Y = S; (**11**) X = S, Y = O

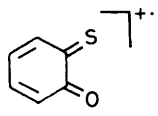
[a] Found 136.0223; C_7H_6NS requires 136.0221.

Scheme 2.

Pyrolysis of both *o*-alkoxy derivatives (**1**) and (**2**) at 750 °C gives a similar distribution of products, with benzoxazole (**14**)

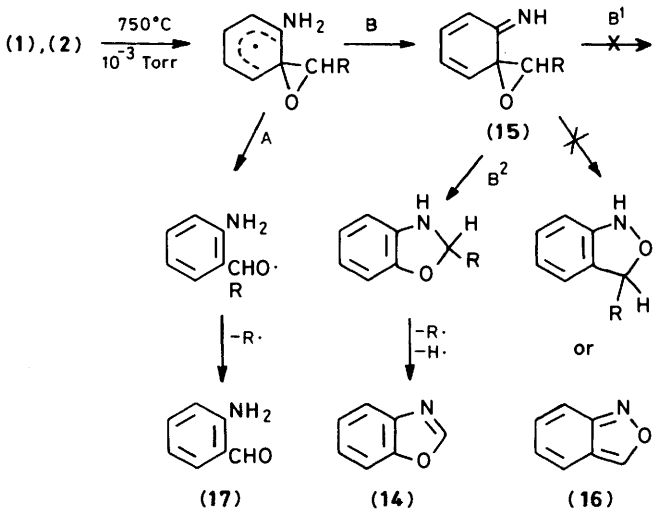
Table 1. Major products (%) from the pyrolyses of 2-methoxy-*N*-allylaniline (**1**) and 2-ethoxy-*N*-allylaniline (**2**)

Products	Precursor (1)	Precursor (2)
Benzoxazole (**14**)	52	56
2-Aminobenzaldehyde (**17**)	12	7
1,2-Benzisoxazole (**18**)	10	7
Aniline	10	3



(13)

present in highest yield (50—60%) (Table 1). The formation of this compound can be rationalised by a process analogous to Scheme 1, route B^2, in which heterocyclisation by C–N bond formation of the intermediate (**15**) is followed by the well-known[5] thermal aromatisation of the dihydro compound (Scheme 3). It is noteworthy that route B is not observed for the

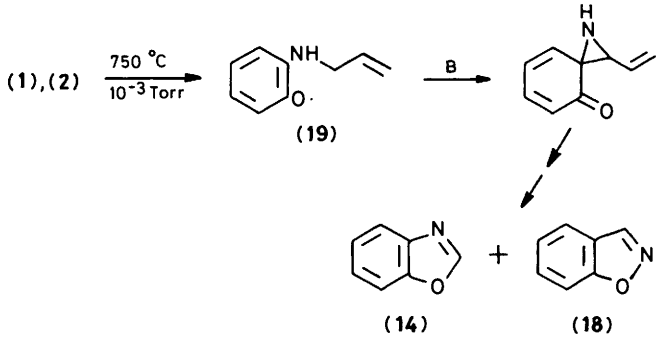


Scheme 3.

case of *o*-alkoxybenzyl radicals.* There is no evidence for cyclisation by N–O bond formation (Scheme 3) though anthranil (**16**), the expected product, is thermally unstable and decomposes to a host of products under the reaction conditions.†

In contrast to the behaviour of the corresponding benzyl radicals,[1] rearrangement by route A to give the aldehyde (**17**) accounts for only 10—20% of the reaction pathway from (**1**) or (**2**). As expected,[1] pyrolysis of the ethoxy derivative (**2**) gave no 2-aminoacetophenone.

One unexpected feature of these reactions was the unambiguous detection (g.l.c. and g.c.–mass spectroscopy) of 1,2-benzisoxazole (**18**) whose formation cannot be explained by the mechanisms of Scheme 3. Although thermal interconversions in the isoxazole–oxazole series are documented,[7] benzoxazole (**14**) is stable under our reaction conditions. The presence of the isoxazole (**18**) may be rationalised by initial *O*-alkyl bond cleavage from (**1**) or (**2**), which can then lead to (**14**) and/or (**18**) by standard route B^2 cyclisation (Scheme 4). Good evidence for

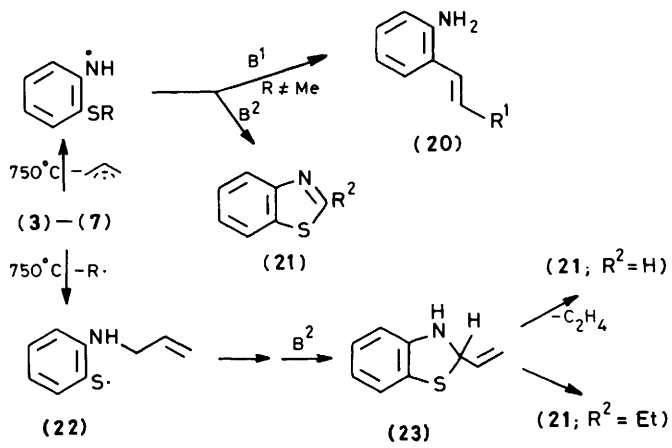


Scheme 4.

analogous *S*-alkyl cleavage is presented below; unfortunately, our attempts to synthesize an authentic source of 2-*N*-alkylaminophenoxyl radicals [*cf.* (**19**)] have been without success.[8]

In common with many pyrolyses, these experiments have also led to relatively small quantities (1—10%) of simple aromatics, notably aniline and quinoline, which are presumably formed by high energy degradation processes. The heterocyclic ring of the quinoline is probably derived from the *N*-allyl group *in toto*: the cyclisation process could be initiated either by generation of an *N*-allyl radical[4] followed by *ipso*-attack and extrusion,[9] or by initial high-energy extrusion of the 2-alkoxy substituent, followed by attack of the resulting aryl radical on the allyl group.

By analogy with the reactions of Scheme 3 and with the earlier work,[1] 2-aminostyrenes (**20**) and benzothiazoles (**21**) would be the expected products from pyrolyses of the 2-alkylthio derivatives (**4**)—(**7**), and this is found to be the case (Scheme 5). The overall ratio of alkene:cyclisation (*cf.* Scheme



Scheme 5.

1 route B^1 : route B^2) is comparable to that of the corresponding benzyl radicals. As might be expected from the low strength of the N–S bond, no isobenzothiazoles were detected. No styrenes

* In view of the present results, we have repeated the pyrolysis of bis-2-methoxybenzyl sulphone[1] and have made a careful search (g.l.c. and g.c.–mass spectroscopy) for benzofuran, the expected product of route B cyclisation. None was found to be present, even as a minor component.

† Substituted anthranils show more controlled thermal behaviour.[6]

Table 2. Major products (%) from the pyrolyses of 2-alkylthio-*N*-allylanilines (**3**)—(**7**)

Products	Precursor (3)	(4)	(5)	(6)	(7)
Benzothiazole (**21**; R^2=H)	7	10	21	17	49
2-Aminostyrene(s) (**20**)		21	(*E*) 12	7	
			(*Z*) 6		
2-Ethylbenzothiazole (**21**; R^2=Et)	2	2	4	4	Trace

Table 3. Major products (%) from the pyrolyses of 2-alkylthio-*O*-allylphenols (**11**)—(**12**)

Products	Precursor (11)		(12)
Benzofuran (**24**)	26		12
2-Hydroxystyrene(s) (**25**)	48	(*E*)	15
		(*Z*)	9

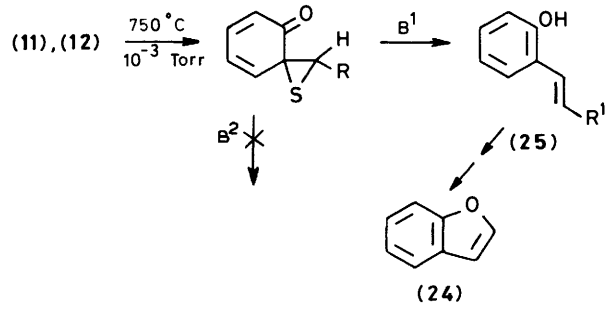
can be formed from the *S*-methyl compound (**3**); whereas sulphur extrusion in the corresponding benzyl series leads to the stable benzocyclobutene, there is considerable evidence that benzazetidines cannot be formed *via* the azaxylylene energy surface.[10] Significantly, the overall accountance is particularly low in this case.

The results from the pyrolysis of the isopropyl compound (**6**) are anomalous. Although the appropriate methylstyrene was obtained, the yield was low, and the major product (also in low yield) was benzothiazole. Route B^2 cyclisation can give only 2-methylbenzothiazole, a compound which was only just detectable (g.l.c. and g.c.–mass spectroscopy) in the crude pyrolysate. In addition, a small quantity of 2-ethylbenzothiazole was detected, which was also present in low yield in the pyrolysates of the related compounds (Table 2), including, significantly, that from the 2-methylthio derivative (**3**). Taken together, these results strongly suggest that *S*-alkyl bond cleavage can take place to generate the 2-*N*-allylthiophenoxyl radical (**22**), which can give the dihydro compound (**23**) by standard route B^2 sequence (Scheme 5). Subsequent vinyl cleavage to give benzothiazole (**21**; R^2=H) may compete with an alternative aromatisation sequence, by hydrogen transfer to the 2-ethyl derivative (**21**; R^2=Et). That the allyl group can, in principle, act as a substrate for hydrogen abstraction by adjacent radicals was proved by a pyrolysis of the *N*,*S*-diallyl derivative (**7**), from which *N*- or *S*-allyl cleavage gave the highest yield of benzothiazole (49%) in the series. 2-Ethylbenzothiazole was also detected (g.l.c.–mass spectroscopy) though its yield was inexplicably low. Thermal cleavage of *S*-isopropyl groups was also demonstrated independently by pyrolysis of 2-isopropylthioaniline; 2-mercaptoaniline was a major product.

Pyrolyses of the tertiary amines (**8**) and (**9**) were complex, though benzothiazole was the major identified component in both cases. The diallyl compound (**9**) gives a significant yield of quinoline (*cf.* above results, and ref. 4).

In one other attempt to generate thiophenoxyl radicals, the *S*-allyl compound (**10**) was pyrolysed, but no significant products could be identified despite a range of conditions. In view of the expected rearrangement to the labile 2-mercaptobenzaldehyde, it is possible that only involatile polymeric products were present after work-up.

Pyrolysis of the *O*-allyl-*S*-alkyl compounds (**11**) and (**12**) was more conventional (Table 3 and Scheme 6) except that no products of cyclisation containing both heteroatoms were detected unambiguously. Nothing is known of the thermal stability of such[11] benzoxathioles, though aromatisation is clearly impossible. However, since a high proportion of the products can be accounted for, especially from (**11**), it seems likely that the reaction is dominated by the alkene pathway (route B^1). The high level of benzofuran (**24**) in both cases can probably be explained by thermal dehydrogenation of the *o*-hydroxystyrene (*c.f.* ref. 1). The *S*-alkyl group is certainly the source of C-2 and C-3 of the benzofuran, since a



Scheme 6.

methylbenzofuran is present (g.l.c.–mass spectroscopy) only in the pyrolysate from the *S*-propyl derivative (**12**).

In conclusion, we have shown in this, and in a previous paper,[1] that hydrogen transfer to benzyl, aminyl and phenoxyl radicals from *ortho*-alkoxy and *ortho*-alkylthio substituents is a quite general process. In all cases, the major products can be rationalised by three variants of a single mechanism (Scheme 1), which involve rearrangement (alkoxy), to give aldehydes, or heteroatom extrusion (alkythio), generally to give alkenes, or heterocyclisation (alkoxy and alkylthio). The relative ratio of the two processes which are open to a given *ortho*-substituent is strongly dependent on the nature of the initial radical.

Experimental

Unless otherwise stated, ^{1}H and ^{13}C n.m.r. spectra were obtained at 100 MHz and 20 MHz respectively for solutions in deuteriochloroform. Ether refers to diethyl ether.

*2-Alkoxy- and 2-Alkylthio-*N*-allylanilines.* (*cf. Ref.* 5).—A solution of the appropriate 2-substituted aniline (0.02 mol) in dimethylformamide (50 ml) containing potassium carbonate (0.02—0.04 mol) was treated with allyl bromide (0.02 mol) and the mixture was stirred at room temperature for 48 h. Water (50 ml) was added, the solution was extracted with ether (3 × 50 ml), and the combined organic extracts were washed with water (4 × 100 ml) to remove any remaining dimethylformamide. The ether extracts were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The required *N*-allyl compound was separated from small amounts of starting material and from an *N*,*N*-diallyl compound, by chromatography on 6% deactivated alumina using light petroleum (b.p. 40—60 °C) [or a mixture of ether (5%) in light petroleum] as eluant. Final purification was effected by bulb-to-bulb distillation. The following compounds were prepared. *2-Methoxy-*N*-allylaniline* (45%), b.p. 90—100 °C (0.1 Torr) [lit.,[12] 80—100 °C (0.01 Torr)]; δ_H 6.6—7.0 (4 H, m), 6.10 (1 H, m), 5.2—5.5 (2 H, m), 4.42 (1 H, br s), 3.92 (3 H, s) and 3.87 (2 H, m); δ_C 146.72 (q), 137.88 (q), 135.45, 121.09, 116.39, 115.77, 110.00, 109.32, 55.22, and 46.10; *m*/*z* 163 (M^+, 100%), 148 (38), 136 (23), 120 (40), and 105 (23); *2-ethoxy-*N*-allylaniline* (74%), b.p. 85—95 °C (0.1 Torr) [lit.,[13] 110 °C (2

Torr)], δ_H 6.6—7.1 (4 H, m), 6.03 (1 H, m), 5.1—5.5 (2 H, m), 4.46 (1 H, br s), 4.12 (2 H, q), 3.86 (2 H, m), and 1.49 (3 H, t); δ_C 145.07 (q), 138.01 (q), 135.57, 120.98, 116.34, 115.64, 110.38, 110.03, 63.56, 46.11, and 14.78; *m/z* 177 (M^+, 100%), 148 (95) and 120 (53); *2-methylthio-N-allylaniline* (64%, from 2-methylthioaniline[14]), b.p. 95—100 °C (0.1 Torr) (Found: C, 66.8; H, 7.15; N, 7.65. $C_{10}H_{13}NS$ requires C, 67.05; H, 7.3; N, 7.8%); δ_H 7.40 (1 H, m), 7.20 (1 H, m), 6.6—6.7 (2 H, m), 5.97 (1 H, m), 5.1—5.4 (2 H, m), 3.85 (2 H, m), and 2.34 (3 H, s); δ_C 147.93 (q), 135.03, 133.85, 129.21, 119.71 (q), 116.96, 115.91, 110.23, 46.11 and 17.33; *m/z* 179 (M^+, 100%), 164 (75), 150 (37), 136 (57), 130 (78), 109 (28), 94 (43), and 77 (25); *2-ethylthio-N-allylaniline* (55%, from 2-ethylthioaniline[15]), b.p. 120—130 °C (0.5 Torr) (Found: M^+, 193.0922. $C_{11}H_{15}NS$ requires M^+ 193.0925); δ_H 6.5—7.5 (4 H, m), 5.92 (1 H, m), 5.0—5.4 (2 H, m), 3.84 (2 H, m), 2.76 (2 H, q), and 1.20 (3 H, t); δ_C 148.85 (q), 135.95, 135.03, 129.70, 117.36, 116.57, 115.79, 110.17, 46.03, 28.84 and 14.73; *m/z* 193 (M^+, 100%), 192 (55), 164 (92), 136 (89), 130 (84), and 109 (34); use of a six-fold excess of allyl bromide and a reaction time of 4 days similarly gave *2-ethylthio-N,N-diallylaniline* (48%), b.p. 105—110 °C (0.1 Torr) (Found: M^+, 233.1239. $C_{14}H_{19}NS$ requires M^+, 233.1239); δ_H 6.9—7.3 (4 H, m), 5.83 (1 H, m), 4.9—5.3 (4 H, m), 3.66 (4 H, m), 2.89 (2 H, q) and 1.36 (3 H, t); *m/z* 233 (M^+, 19%), 192 (100), 136 (81), 130 (52), and 109 (24); similarly, alkylation of 2-ethylthio-*N*-allylaniline with methyl iodide gave *2-ethylthio-N-allyl-N-methylaniline* (69%), b.p. 105—110 °C (0.5 Torr) (Found: M^+, 207.1081. $C_{12}H_{17}NS$ requires M^+, 207.1082); δ_H 6.2—7.5 (4 H, m), 5.78 (1 H, m), 4.7—5.3 (2 H, m), 3.56 (2 H, m), 2.78 (2 H, q), 2.58 (3 H, s) and 1.24 (3 H, t); *m/z* 207 (M^+, 45%), 206 (64), 193 (56), 192 (56), 178 (83), 164 (68), and 136 (100); *2-propylthio-N-allylaniline* (62%, from 2-propylthioaniline[16]), b.p. 115—120 °C (0.2 Torr) (Found: C, 69.55; H, 8.05; N, 6.85. $C_{12}H_{17}NS$ requires C, 69.5; H, 8.25; N, 6.75%); δ_H 7.1—7.5 (2 H, m), 6.5—6.7 (2 H, m), 5.95 (1 H, m), 5.1—5.4 (2 H, m), 3.85 (2 H, m), 2.70 (2 H, t), 1.60 (2 H, m), and 1.00 (3 H, t); δ_C 148.78 (q), 135.83, 135.04, 129.62, 117.81 (q), 116.62, 115.85, 110.19, 46.09, 36.95, 22.83, and 13.16; *m/z* 207 (M^+, 100%), 164 (90), 136 (82), 130 (80), and 124 (60); *2-isopropylthio-N-allylaniline* (40%, from 2-isopropylthioaniline[16]), b.p. 95—100 °C (0.1 Torr) (Found: C, 69.25; H, 8.0; N, 7.0. $C_{12}H_{17}NS$ requires C, 69.5; H, 8.25; N, 6.75%); δ_H 7.39 (1 H, m), 7.20 (1 H, m), 6.5—6.7 (2 H, m), 5.95 (1 H, m), 5.1—5.4 (2 H, m), 3.81 (2 H, m), 3.16 (1 H, septet), and 1.23 (6 H, d); δ_C 149.52 (q), 137.18, 135.08, 130.06, 116.95 (q), 116.45, 115.78, 110.19, 46.07, 38.62, and 23.19; *m/z* 207 (M^+, 100%), 164 (93), 136 (65), 130 (59), 124 (93), and 109 (24); *2-allylthio-N-allylaniline* (20%, from 2-allylthioaniline[17]), b.p. 110—120 °C (0.2 Torr) (Found: C, 70.1; H, 7.6; N, 7.05. $C_{12}H_{15}NS$ requires C, 70.2; H, 7.35; N, 6.8%); δ_H 7.0—7.5 (2 H, m), 6.5—6.7 (2 H, m), 5.88 (2 H, m), 4.8—5.4 (4 H, m), 4.70 (1 H, br s), 3.83 (2 H, m) and 3.33 (2 H, m); δ_C 148.98 (q), 136.48, 134.97, 133.78, 130.01, 117.10, 116.80 (q), 116.57, 115.86, 110.25, 46.06 and 38.05; *m/z* 205 (M^+, 70%), 164 (81), 136 (100), 130 (93), 124 (63), and 109 (37).

2-Alkoxy-S-alkylthiophenols.—The appropriate 2-hydroxy-*S*-alkylthiophenol was prepared by a literature method from 2-hydroxythiophenol.[18] The second alkylation was accomplished under the above conditions, using the alkyl halide in dimethylformamide containing potassium carbonate. Purification by chromatography was not required. The following compounds were obtained. *2-Ethoxy-S-allylthiophenol* (60%, from 2-hydroxy-*S*-allylthiophenol[19]), b.p. 85—95 °C (0.1 Torr) (Found: M^+, 194.0758. $C_{11}H_{14}OS$ requires M^+, 194.0765); δ_H 6.7—7.5 (4 H, m), 5.89 (1 H, m), 4.9—5.3 (2 H, m), 4.08 (2 H, q), 3.05 (2 H, m), and 1.49 (3 H, t); δ_C 156.83 (q), 133.63, 130.12, 127.14, 120.62, 117.24, 111.46, 64.00, 35.15, and 14.63 (one quaternary carbon signal not apparent); *m/z* 194 (M^+, 100%), 165 (17), 137 (34), 132 (20), 124 (45) and 97 (38); *2-allyloxy-S-ethylthiophenol* (80%, from 2-hydroxy-*S*-ethylthiophenol[18]), b.p. 100—110 °C (0.5 Torr) (Found: C, 67.95; H, 7.0. $C_{11}H_{14}OS$ requires C, 68.0; H, 7.25%); δ_H 6.7—7.4 (4 H, m), 6.06 (1 H, m), 5.2—5.6 (2 H, m), 4.60 (2 H, m), 2.91 (2 H, q), and 1.26 (3 H, t); δ_C 155.84 (q), 132.81, 128.51, 126.23, 120.94, 117.03, 114.44 (q), 111.76, 68.98, 25.53, and 13.79; *m/z* 194 (M^+, 81%), 165 (50), 153 (100), 125 (88), 97 (92), 94 (46), and 91 (65); *2-allyloxy-S-propylthiophenol* (68% from 2-hydroxy-*S*-propylthiophenol[18]), b.p. 100—105 °C (0.1 Torr) (Found: C, 69.4; H, 7.6. $C_{12}H_{16}OS$ requires C, 69.2; H, 7.75%); δ_H 6.7—7.4 (4 H, m), 6.02 (1 H, m), 5.2—5.6 (2 H, m), 4.58 (2 H, m), 2.84 (2 H, t), 1.70 (2 H, m) and 1.00 (3 H, t); δ_C 155.94 (q), 132.86, 128.62, 126.21, 120.97, 117.07, 114.48 (q), 111.80, 69.03, 33.63, 22.10, and 13.31; *m/z* 208 (M^+, 48%), 167 (24), 125 (100), and 97 (29).

Pyrolysis Experiments.—Small-scale (0.5—1 mmol) pyrolyses were carried out as previously described.[20] Unless otherwise stated, products were identified by comparison (g.l.c. and g.l.c.–mass spectroscopy using columns of 5% Carbowax 20M or 5% SE30) with authentic samples. Yields of major products were obtained from the ^{1}H n.m.r. spectrum of the crude pyrolysate using cyclohexane (5 µl) as an integral calibrator. Yields of minor products were generally estimated from the relative areas of g.l.c. peaks. Results are presented as follows: compound pyrolysed, quantity, inlet temperature, furnace temperature, pressure range, pyrolysis time, and products, with their yields and parent ions from g.l.c.–mass spectrometry.

2-Methoxy-N-allylaniline, 0.160 g (0.98 mmol), 70 °C, 750 °C, 20—1 × 10^{-3} Torr, 15 min; aniline (*ca.* 10%), *m/z* 93; *N*-methylaniline (trace), *m/z* 107; *o*-toluidine (trace), *m/z* 107; benzoxazole (52%), *m/z* 119; 1,2-benzisoxazole (*ca.* 10%) *m/z* 119; 2-aminobenzaldehyde (12%), *m/z* 121 [identified by comparison of the ^{1}H n.m.r. chemical shift of the aldehyde proton (δ_H 9.81) with a literature value[21] (δ_H 9.77)]; quinoline (trace) *m/z* 129 and methylquinoline (trace), *m/z* 143. 2,1-Benzisoxazole (anthranil), was unambiguously absent (g.l.c.).

2-Ethoxy-N-allylaniline, 0.183 g (1.03 mmol), 70 °C, 750 °C, 1—5 × 10^{-3} Torr, 15 min; aniline (*ca.* 3%), *m/z* 93; benzoxazole (56%), *m/z* 119; 1,2-benzisoxazole (*ca.* 7%), *m/z* 119; 2-aminobenzaldehyde (7%), *m/z* 121 (identified as above); quinoline (trace), *m/z* 129, and methylquinoline (trace), *m/z* 143. Anthranil was unambiguously absent (g.l.c.).

2-Methylthio-N-allylaniline, 0.180 g (1.0 mmol), 60 °C, 750 °C, 1—5 × 10^{-3} Torr, 20 min; *o*-toluidine (trace) *m/z* 107; 2-methylthioaniline (4%), *m/z* 139; quinoline (trace) *m/z* 129; benzothiazole (7%), *m/z* 135 and 2-ethylbenzothiazole (2%), *m/z* 163.

2-Ethylthio-N-allylaniline, 0.111 g (0.58 mmol), 50 °C, 750 °C, 10^{-3} Torr, 15 min; indole (1%) *m/z* 117; 2-aminostyrene (21%), *m/z* 119 [identical (g.l.c.) with an authentic sample, prepared in low yield by pyrolysis of the sodium salt of 2-aminoacetophenone tosylhydrazone (*cf.* reference 5)]; benzothiazole (10%), *m/z* 135; 2-methylbenzothiazole (trace) *m/z* 149; 2-ethylbenzothiazole (2%), *m/z* 163 and recovered starting material (2%), *m/z* 193.

2-Propylthio-N-allylaniline, 0.178 g (0.86 mmol), 60 °C, 750 °C, 1—5 × 10^{-3} Torr, 25 min: *Z*-β-methyl-2-aminostyrene (6%), *m/z* 133; *E*-β-methyl-2-aminostyrene (12%), *m/z* 133; benzothiazole (21%), *m/z* 135 and 2-ethylbenzothiazole (4%), *m/z* 163. The aminostyrenes were identified by comparison of the ^{1}H n.m.r. spectra with literature data.[22]

2-Isopropylthio-N-allylaniline, 0.143 g (0.69 mmol), 60 °C, 750 °C, 1—5 × 10^{-3} Torr, 15 min; α-methyl-2-aminostyrene (7%), *m/z* 133; benzothiazole (17%), *m/z* 135 and 2-ethylbenzothiazole (4%), *m/z* 163. Only a trace of 2-methylbenzothiazole (*m/z* 149) was detected (g.c.–mass spectroscopy).

2-*Allylthio*-N-*allylaniline*, 0.102 g (0.50 mmol), 100 °C, 750 °C, 10^{-3} Torr, 15 min; benzothiazole (49%), *m/z* 135; 2-methylbenzothiazole (trace), *m/z* 149 and 2-ethylbenzothiazole (trace), *m/z* 163.

2-*Ethylthio*-N,N-*diallylaniline*, 0.134 g (0.58 mmol), 60 °C, 750 °C, 10^{-3} Torr, 25 min; quinoline (3%), *m/z* 129 and benzothiazole (5%), *m/z* 135. Several very minor components were not identified.

2-*Ethylthio*-N-*allyl*-N-*methylaniline*, 0.075 g (0.36 mmol), 60 °C, 750 °C, 1—5 × 10^{-3} Torr, 20 min: 2-(methylamino)styrene (7%), *m/z* 133 and benzothiazole (13%), *m/z* 135. Several minor components were not identified.

2-(*Isopropylthio*)*aniline*, 0.075 g (0.45 mmol), 40 °C, 750 °C, 10^{-3} Torr, 20 min; g.l.c. analysis showed two products, one of which was 2-mercaptoaniline by comparison with an authentic sample. No starting material remained (^{1}H n.m.r.) under these pyrolysis conditions.

2-*Ethoxy*-S-*allylthiophenol*, 0.165 g (0.85 mmol), 50 °C, 750 °C, 1—5 × 10^{-3} Torr, 20 min; an extremely complex mixture was obtained, from which the following components were identified; phenol, *m/z* 94; styrene *m/z* 104; benzofuran, *m/z* 118; acetophenone, *m/z* 120 and *o*-thiocresol, *m/z* 124. A signal at δ9.82 in the ^{1}H n.m.r. spectrum of the pyrolysate may be attributable to the unstable[23,24] 2-mercaptobenzaldehyde, but this could not be corroborated by g.l.c.–mass spectroscopy. Pyrolysis at 600 °C gave an even more complex mixture (at least fourteen components); a furnace temperature of 450 °C gave predominantly recovered starting material.

2-*Allyloxy*-S-*ethylthiophenol*, 0.118 g (0.61 mmol), 60 °C, 750 °C, 10^{-3} Torr, 20 min; benzofuran (*ca.* 26%), *m/z* 118 and *o*-hydroxystyrene (48%), *m/z* 120 (identical with an authentic sample prepared in low yield by pyrolysis of the sodium salt of *o*-hydroxyacetophenone tosylhydrazone[5]).

2-*Allyloxy*-S-*propylthiophenol*, 0.103 g (0.50 mmol), 60 °C, 750 °C, 10^{-3} Torr, 20 min; styrene (trace), *m/z* 104; benzofuran (*ca.* 12%), *m/z* 118; methylbenzofuran (tentative, trace), *m/z* 132; phenyl allyl ether (tentative, trace), *m/z* 134; *Z*-2-hydroxy-β-methylstyrene (9%), *m/z* 134 and *E*-2-hydroxy-β-methylstyrene (15%), *m/z* 134. The 2-hydroxystyrenes were identified by comparison with literature ^{1}H n.m.r. spectra.[25]

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