Homolytic Aromatic Substitution by Heterocyclic Free Radicals. Part II.[1] Reaction of Thiazol-2-yl and Benzothiazol-2-yl Radicals with Aromatic Compounds

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Free-radical aromatic substitution by thiazol-2-yl radicals was carried out with variously substituted aromatic compounds. The thiazol-2-yl radical was generated by photolysis of 2-iodothiazole, or by thermal decomposition of the diazonium salt of 2-aminothiazole. The isomeric ratios and the relative rates of substitution were determined and compared with those obtained with phenyl radicals. These data confirmed the electrophilic character of the radical. The major by-products in the photolysis were identified as 3-arylisothiazoles from rearrangement of 2-arylthiazoles. Results describing the free-radical benzothiazolylation of alkylbenzenes (R = Me, Et, Pr^i, and Bu^t) are also reported. From these results the benzothiazol-2-yl radical appears to be more electrophilic than the thiazol-2-yl radical.

FROM their reactivities in aromatic substitution, free radicals [1-4] can be classified as electrophilic, nucleophilic, or neutral depending on the structure, or on the nature of the substituting groups. For instance, cyclohexyl,[5] methyl,[6-12] and benzyl [13-15] radicals are nucleophilic whereas trichloromethyl,[16] triphenylmethyl,[4] substituted phenyl,[17-21] oxygen-containing radicals,[22] and heteroaromatic radicals [23-26] are electrophilic to some extent.

Since the thiazol-2-yl radical has recently been shown to be weakly electrophilic,[1] we sought to extend the results from the alkylbenzenes [1] to other aromatic substances such as halogenobenzenes, anisole, benzonitrile, methyl benzoate, and nitrobenzene. We also examined the reactivity of the alkylbenzenes (R = Me, Et, Pr^i, and Bu^t) towards benzothiazol-2-yl radical.

Among several methods used to generate the thiazol-2-yl and benzothiazol-2-yl radicals we chose the alkaline decomposition of diazonium solutions of heterocyclic amines [27-32] and the photochemical decomposition of the appropriate iodothiazole or benzothiazole.[26,33-36] Another method used in the thiophen [37-39] and thiazole series [40] was the thermal decomposition of the corresponding heterocyclic peroxide. Although thiazol-2-yl peroxide leads to 2-arylthiazoles in good yield (23—55%), with other heterocyclic peroxides major products were esters and acids derived from the related acyloxy-radicals which were not decarboxylated. This method is too difficult on a large scale. 2-Arylthiazoles have been also obtained by silver oxide oxidation of the thiazol-2-ylhydrazine [40] in solution in benzene, bromobenzene, and cumene, but with a lower yield (*ca.* 10%).

RESULTS AND DISCUSSION

Isomer Ratios and Relative Rates of Substitution.—The irradiation of 2-iodothiazole (1) or the alkaline decomposition of the diazonium salt of the 2-aminothiazole (2) gave the thiazol-2-yl radical (3), the presence of which

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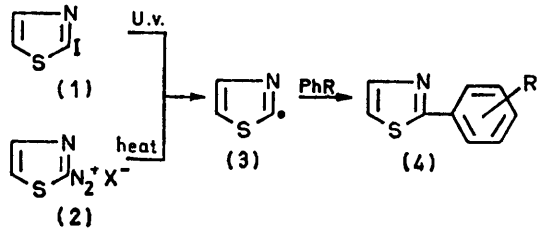
was shown by the formation of mixtures of substituted 2-arylthiazoles (4) when the decomposition is carried



SCHEME

out in aromatic solvents (Scheme). Table 1 shows the experimental isomer distributions for free-radical thiazol-2-ylation together with corresponding data on phenylation for similar experimental conditions. These results were determined by g.l.c., and were in each case the average of at least two independent runs. During the Gomberg reaction 2-arylthiazoles were produced in low yield (*ca.* 10%) whereas during the photolysis of 2-arylthiazoles higher yields were obtained (50—60%).

In order to obtain the reactivities of aromatic substrates relative to benzene, competitive experiments were carried out. Thiazol-2-yl radicals were generated by photochemical decomposition of the 2-iodothiazole in an excess of an equimolar mixture of aromatic substrate and benzene. The reactions were directly analysed by g.l.c. and the amounts of *ortho*-, *meta*-, and *para*-substituted 2-phenylthiazole were determined by use of biphenyl or *p*-bromobiphenyl as internal standards.

The partial rate factors of *ortho*-, *meta*-, and *para*-positions of these substrates, relative to a single position of benzene, were derived in the usual manner (Table 2) from isomer ratios and rates relative to benzene.[2,41-44]

TABLE 1

Experimental isomer distribution for free-radical thiazol-2-ylation and phenylation

		Isomers ratios						
		Phenylation				Thiazol-2-ylation		
Aromatic compounds	Source of radicals [a]	*o*	*m*	*p*	Sources of radicals	*o*	*m*	*p*
Toluene	U.v.	65·5	20·0	14·5	U.v.	69·0	18·0	13·0
					U.v.[c]	60·0	23·0	17·0
	G	65·0	19·8	15·2	G	71·0	16·5	12·5
Chlorobenzene	U.v.	58·0	26·5	15·5	U.v.	48·5	32·5	19·0
	G	55·0	28·5	16·5	G	50·0	31·5	18·5
Bromobenzene	U.v.	60·0	25·7	14·3	U.v.	47·5	33·5	19·0
	G	58·0	26·3	15·7	G	46·0	34·0	20·0
	P + Cu 130 °C	56·0	28·0	16·0	P [d]	50·0	31·6	81·4
Anisole	U.v.	71·5	15·0	13·5	U.v.	63·0	14·0	23·0
	G	73·0	14·0	13·0	G	65·0	10·0	25·0
Methyl benzoate	U.v.	54·0	19·0	27·0	U.v.	54·0	20·4	25·6
	P + Cu 130 °C	60·5	17·2	22·3	G	54·0	19·0	27·0
Benzonitrile	U.v.	52·5	17·5	30·0	U.v.	56·0	18·0	26·0
	P + Cu 130 °C	61·8	14·2	24·0				
Nitrobenzene	G	60·0	10·5	29·5	G	60·0	14·5	25·5
	P + Cu 130 °C	56·0	15·5	28·5				
	P 80 °C	62·5	11·7	26·8				

[a] U.v., photochemical decomposition of iodobenzene, or 2-iodothiazole. Irradiation was performed with a SP 500 W lamp for 30—60 min at 60—80 °C; G, thermal decomposition of the diazonium salt of aniline, or 2-aminothiazole for 24 h at 0—20 °C; P, thermal decomposition of benzoyl peroxide at 80 °C. [b] These values agree with those reported in the literature either by thermal decomposition of benzoyl peroxide or by photochemical decomposition of iodobenzene (Table 2). [c] By photochemical decomposition of 2-bromothiazole. In this case it seems that dihydro-compounds were also produced by disproportionation and these side reactions will be selective. [d] Ref. 40.

TABLE 2

Relative reactivities ($_xk$), and partial rate factors (f_i) in homolytic aromatic substitution at 80—100 °C

		Phenylation				Thiazol-2-ylation				
Aromatic compounds	k_{Ph}	f_o	f_m	f_p	f_m/f_p	$k_{2\text{-Th}}$	f_o	f_m	f_p	f_m/f_p
Toluene	1·65 [a]	3·2	1	1·4	0·69	2·1	4·3	1·13	1·64	0·69
Chlorobenzene	1·4 [b]	2·4	1·1	1·3	0·86	0·9	1·3	0·88	1·02	0·87
Bromobenzene	1·12 [c]	2	0·86	0·96	0·86	0·7	1	0·7	0·8	0·9
Anisole	1·85 [d]	4	0·83	1·5	0·58	2·2	4·16	0·92	3·03	0·30$_7$
Methyl benzoate	2·4 [e]	3·9	3·37	3·9	0·34	1·75	2·83	1·07	2·7	0·4
Benzonitrile	3·5 [f]	5·5	1·83	6·3	0·25	2·0	3·36	1·08	3·1	0·34$_6$
Nitrobenzene	3·0	5·6	1·05	4·8	0·2	1·5	4·5	0·65	2·3	0·28

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Relative reactivities and partial rate factors are more indicative of radical reactivity than isomer ratios.

Thus, with aromatic compounds bearing electron-attracting groups (X = $MeCO_2$, CN, or NO_2) relative reactivities decrease in the order $k_{2\text{-Th}} < k_{Ph}$ while the $f_m : f_p$ ratios increase.

The reverse effect is observed in the case of electron-releasing groups (X = Me or MeO). These results suggest an electrophilic character for thiazol-2-yl radicals. If these values are compared with those reported by Tiecco *et al.*[23,24] for 2- and 3-thienyl radicals, a similar weak electrophilic character is observed for thiazol-2-yl and 3-thienyl radicals. These observations show that in thiazol-2-yl radicals the inductive electron-attraction of the sulphur heteroatom is greatly reduced by the presence of the nitrogen atom of the thiazole ring.

The isomer ratios and relative rates for homolytic benzothiazol-2-ylation are in Table 3. As for the

TABLE 3

Isomer ratios and relative rates for homolytic thiazol-2-ylation and benzothiazol-2-ylation of alkylbenzenes [a]

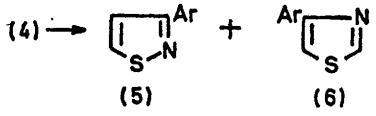
Substrates	Radicals	Isomer ratios (%) o	m	p	Reactivity rel. to C_6H_6
Toluene	Benzothiazol-2-yl	67·5	17·7	14·8	3·20
	Thiazol-2-yl	69·0	18·0	13·0	2·10
Ethylbenzene	Benzothiazol-2-yl	58·0	23·7	18·3	2·00
	Thiazol-2-yl	64·0	21·1	14·9	1·70
Isopropyl-benzene	Benzothiazol-2-yl	48·9	31	20·1	1·70
	Thiazol-2-yl	45·0	36·0	19·0	1·40
t-Butylbenzene	Benzothiazol-2-yl	36·0	41·5	22·5	1·45
	Thiazol-2-yl	31·0	45·5	23·5	1·05

[a] The isomer ratios were almost the same whatever the radical source. In the photolysis of 2-iodobenzothiazole no isomerization products were detected.

thiazol-2-yl radicals[1] and thienyl radicals[23,25] the isomer distribution was not very different from that reported for phenyl radical. However, the relative rates show slight modifications which can be attributed to the electrophilic character of these heteroaromatic radicals. Moreover in this case the benzene part of the benzothiazole behaves like a withdrawing group as in the 3-benzo[*b*]thienyl radical.[25] This is exemplified by comparison with the thiazol-2-yl radical, which is less electrophilic than the benzothiazol-2-yl radical.

Side Reactions.—In the reaction mixtures by-products were obtained besides 2-arylthiazoles. Most of them were identified by t.l.c., g.l.c., and n.m.r. In all cases, in the Gomberg reaction about 10% of 2,2′-bithiazolyl are formed with small amounts of thiazole, and of dyes, but in u.v. irradiation the main side reaction is the photochemical rearrangement of 2-arylthiazoles initially formed. These photoisomers have been identified as 3-arylisothiazoles (5) and 4-arylthiazoles[45-48] (6).

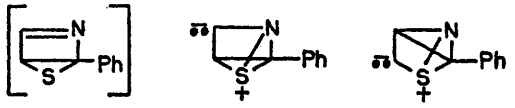
With a Philips HPL 125 W, Hanau Q 81, or PQ 150 W high-pressure lamps and an irradiation time of 24 h, there was a high percentage of by-products. For this reason, in competitive experiments, we preferred to use



(5) (6)

a Philips SP 500 W lamp with an irradiation time of 30 min. In such conditions, less of the 3-arylisothiazoles was found (10—15%) while the 4-arylthiazoles were present in traces only. The amounts of photoisomers were accounted for in the determination of the relative reactivity.

Such photochemical isomerizations of heteroaromatic compounds have been widely studied.[49] The mechanism of these photorearrangements is not clear, but a valence-bond tautomer (7) or a tricyclic sulphonium ion [(8) or (9)] have been suggested as the most probable



(7) (8) (9)

intermediates.[45,46] In the photochemical benzothiazolylation no photoisomer was found (*i.e.*, photolysis of 2-phenylbenzothiazole does not lead to 2-phenylbenzoisothiazole).

In the halogenobenzene series, the composition of the main reaction products is summarized in Table 4.

TABLE 4

Products from irradiation of 2-iodothiazole in halogenobenzenes (in competition with benzene) [a]

Products	Substrates: Chlorobenzene (%)	Bromobenzene (%)
Biphenyl [c]	10	30
2-Phenylthiazole	25	26·4
3-Phenylisothiazole [d]	16	6·6
Halogenobiphenyl [e]	8	20
	o = 40, m + p = 60	o = 60, m + p = 40
2-Halogenophenylthiazoles	36	12
	o = 47	o = 45
	m + p = 53	m + p = 55
3-Halogenophenylisothiazoles [d]	5	5
	o = 46, m + p = 53	o = 40, m + p = 60

[a] By photolysis 24 h with 0·81 W or HPL 125 W lamps, 100 mg of 2-iodothiazole in an equimolar mixture of chlorobenzene or bromobenzene and benzene (0·1 mol). [b] With iodobenzene major products were biphenyl, iodobiphenyl (o = 62·5%, m + p = 37·5%), and iodoterphenyl. [c] With *ca.* 2—3% of 1,4-dihydrobiphenyl both arising from homolytic substitution of phenyl radicals on benzene, or by disproportionation of intermediate phenylcyclohexadienyl. [d] With traces of 4-phenylthiazole or 4-halogenothiazoles. [e] These isomers were closer to those obtained by photolysis of halogenobenzenes alone.

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Besides photoisomers, a large amount of halogenobiphenyls arising from homolytic substitution of these substrates by phenyl radicals were formed.

Chlorobiphenyl isomer ratios in this reaction were different from those obtained with other sources of phenyl radicals, *i.e.*, photochemical decomposition of iodobenzene or thermal decomposition of benzoyl peroxide. This may be due to disproportionations or dimerizations of intermediate *o*-chlorocyclohexadienyl–phenyl σ complexes in the absence of oxidizing radicals.

In these reactions the 2-phenylthiazole (traces only) arising from dimerization of phenyl and thiazol-2-yl radicals were also present. With anisole as substrate, iodoanisole reported by Tiecco *et al.*[23,25] was observed among other products. During the photolytic decomposition in alkylbenzenes bearing α hydrogen atoms, dimers arising from the photolysis of the substrate with traces of oxygen were obtained.

EXPERIMENTAL

General Work-up for Thiazolylation, Benzothiazolylation, and Phenylation.—Decomposition of the heterocyclic diazonium salt. Commercial 2-aminothiazole (5 g, 0·05 mol) from Fluka A.G., Buchs S.G. (m.p. 89—91 °C) was dissolved in 12N-hydrochloric acid (40 cm³) and diazotized by addition of a concentrated aqueous solution of sodium nitrite (3·4 g, 0·05 mol). The temperature was maintained between −5 and +5 °C. The diazonium solution was added dropwise to the mixture of monosubstituted benzene (5 mol) and 2N-sodium hydroxide (200 cm³). Stirring was continued for an additional 20 h at room temperature. The organic layer was separated, and the remaining solution extracted with ether. The extracts were dried (Na_2SO_4) and the excess of ether and substrate removed under vacuum. The residues were then analysed first by g.l.c., and then crude 2-arylthiazoles were separated from by-products by t.l.c. and re-chromatographed. In the case of benzothiazol-2-ylation, it was necessary to use a larger volume of hydrochloric acid to dissolve the 2-aminobenzothiazole.

With complex mixtures in which substitution products were present in minor amounts, 2-aryl products were separated from the crude mixtures by concentrated hydrochloric acid extraction. A more accurate isomer ratio and relative rate factors were thus obtained.

Photochemical decomposition of 2-iodothiazole, 2-iodobenzothiazole, or iodobenzene. 2-Iodothiazole was synthesized [50,51] by two literature methods. It is a yellow oil which solidified on cooling (b.p. 116 °C at 40 mmHg). 2-Iodobenzothiazole (60%), m.p. 78 °C, was obtained following Iversen [51] by the action of iodide on the lithium derivative of 2-benzothiazole.

Solutions of the 2-iodo-derivative (0·01 mol) in the monosubstituted benzene (0·1 mol) were put into a cylindrical quartz tube (2 × 10 cm) and irradiated for 20—30 min with a Philips SP 500 W high-pressure mercury lamp. After reaction, excess of iodine was removed by washing with sodium thiosulphate solution. The organic layer was dried (Na_2SO_4) and worked-up as above.

In larger scale experiments, other lamps (Philips HPL, 125 W, or Hanau Q 81, or PQ 150 W) were used. In this case, irradiation time was 24 h.

Photochemical isomerization of 2-phenylthiazole. 2-Phenylthiazole (100 mg) and iodine (traces) in benzene (30 cm³) were irradiated for 90 min as described above. The excess of benzene was removed by distillation, and the residue analysed by g.l.c. with biphenyl as internal standard. 3-Phenylisothiazole (40% yield) and 4-phenylthiazole (2·5% yield) were the main products. Biphenyl (2·4%) and 1,4-dihydrobiphenyl (1·6%) were also formed among other unidentified products. Without iodine, 4-phenylthiazole was obtained in 46·5% yield with a little 3-phenylisothiazole (3·5%). By irradiation for 24 h with other high-pressure mercury lamps, 2-phenylthiazole gave 3-phenylisothiazole as the major photolysis product but with a lower yield (*ca.* 12—15%). In this case polymers were formed in high yield (*ca.* 50%). These reactions have been extended to other monosubstituted 2-phenylthiazoles.[48]

Competitive experiments. Competitive runs were carried out in duplicate with an equimolar amount of benzene and monosubstituted benzene. A large excess of both was used to avoid the formation of disubstitution products. The work-up was as described above.

Synthesis.—2-Arylthiazoles. Some 2-arylthiazoles were synthesized by Hantzsch's method.[52-54] Appropriately substituted thiobenzamides were refluxed with three-fold excess of chloroacetaldehyde for 10 h. The solution was then evaporated, ether and aqueous sodium carbonate added, and the ether extracts dried and worked up to give the crude 2-arylthiazoles. The yield of 2-arylthiazoles ranged from 40 to 75% depending on the substrate.

Purified products were obtained either by preparative g.l.c., t.l.c., or by coupling g.l.c. and t.l.c. M.p.s or b.p.s were in the range reported in the literature: 2-phenylthiazole [40,52-54] (b.p. 133—134 °C at 20 mmHg, picrate, m.p. 126 °C), 2-*o*-tolylthiazole [53] (b.p. 115—116 °C at 5 mmHg, picrate, m.p. 108 °C), 2-*m*-tolylthiazole (b.p. 150—160 °C at 20 mmHg), 2-*p*-tolylthiazole [55] (b.p. 160—165 °C at 20 mmHg, picrate, m.p. 160 °C), 2-*p*-chlorophenylthiazole [53] (m.p. 39—40 °C, picrate, 155—156 °C), 2-*p*-methoxyphenylthiazole (m.p. 55—56 °C), 2-*p*-bromophenylthiazole [40,55] (m.p. 51—52 °C, picrate, m.p. 161—162 °C).

Another route to 2-*p*-bromophenylthiazoles was found in brominating the 2-phenylthiazole (1·25 g) with excess of bromine [2 cm³ in the presence of $AgSO_4$ (8 g) (traces)]. The major product was 5-bromo-2-*p*-bromophenylthiazole. 2-*p*-Nitrophenylthiazole was prepared by nitration of the 2-phenylthiazole.[56,57] G.l.c. analysis (on silicone oil column at 200 °C) of the yellow crystalline product showed 2-*p*-nitrophenylthiazole (89%) with minor components, 2-*o*-nitrophenylthiazole (3%), and 2-*m*-nitrophenylthiazole (8%).[58] Pure 2-*p*-nitrophenylthiazole (m.p. 147—148 °C;

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lit.,[54,59] 148 °C) was obtained by recrystallization from benzene–cyclohexane. 2-*o*-Nitrophenylthiazole was separated from its 2-*para*-isomer by coupling g.l.c. with t.l.c. by use of Instermat I.G.C. 12 and Camag–Diochrom instruments.

Thiobenzamides. Thiobenzamides were prepared as described in the literature by two different ways: either by S ⟶ O exchange between the corresponding benzamide, by use of phosphorus pentasulphide in pyridine (or dioxan) solution and in the presence of magnesium carbonate,[60] or by the action of H_2S on the appropriate nitrile with pyridine and triethylamine as solvents.[61,62] In this reaction thioacetamide in an acidic medium can also be used as an H_2S generator, dimethylformamide being the solvent.

2-Arylbenzothiazoles. 2-Arylbenzothiazoles were obtained by reaction of various substituted (R = Me, Et, Pr^i, or Bu^t) benzoyl chlorides with *o*-aminothiophenol.[63,64] In some cases a zinc salt was necessary.[65]

Some 2-arylthiazoles and 2-arylbenzothiazoles were also prepared by thermal decomposition of the corresponding aroyl peroxides in thiazole or benzothiazole in an acidic medium.[66] In these cases the 2-isomer was the major product and further purification were carried out by t.l.c.

Aromatic derivatives. The following materials were commercial. Biphenyl (m.p. 69—70 °C), bibenzyl (m.p. 50—51 °C), diphenylmethane (m.p. 26—27 °C), several monosubstituted biphenyls, all three bromobenzonitriles from Aldrich, and chlorobenzonitriles from Fluka.

A mixture of methylphenyl(phenyl)methanes was prepared by the reaction of toluene with benzyl chloride and $AlCl_3$.[5] Bicumyl (m.p. 117 °C) and 1,2-dimethyl-1,2-diphenylethane were prepared by photolytic (or thermal) decomposition of di-t-butyl peroxide in corresponding alkylbenzenes by Schmetlik's method.[67]

Analytical Methods.—G.l.c.[68] A Hy Fi model 600 C chromatograph with flame ionization was used for analysis. Preparative g.l.c. was performed on a Carlo Erba (Fractovap model G.P.) instrument. An Intersmat I.G.C. 12 was used in conjunction with the Camag–Dichrom apparatus for g.l.c.–t.l.c.

(i) *Qualitative analysis of the reaction mixture.* Suitable columns for the separation of the expected isomeric 2-arylthiazoles were found by trial. Only the isomeric 2-halogenophenylthiazoles and 2-methoxyphenylthiazoles could not be resolved completely; although substituted 2-*o*-phenylthiazoles could be resolved easily, the *meta*- and *para*-isomers were chromatographically indistinguishable on our columns. In these cases g.l.c. gave the ratio of *o*- : *m*- + *p*- (unresolved) but isolation of the isomer mixture by preparative g.l.c. or t.l.c. enabled the *meta* : *para* ratio to be determined by quantitative i.r. or n.m.r. analysis.

All other reaction mixtures were resolved on 6—10 ft × ⅛ in, 5—10% 4000 (A) or 20 M (A′) Carbowax, Silicone oil SE 30 (B) or QF-1 (B′), and Apiezon L (C) on 80—100 mesh A.W. DMCS chromosorb G or W columns. Oven temperatures were 180—220 °C. The upper temperature limit of the stationary phases of the first two columns enable them to be used for analysis of 2-arylbenzothiazoles.

The components of a reaction mixture were identified by comparing their retention time with those of authentic samples. This was further confirmed by collecting the compound by preparative g.l.c. or t.l.c. and determining its n.m.r. spectrum and comparing it with that of the authentic sample. Where authentic samples were not available the compound was identified by a chromatographic method based on Martin's principle [69] by use of the relative retention volumes or Kováts indices.[70]

(ii) *Quantitative analysis by g.l.c. Isomer ratios.* On 4000 or 20 M Carbowax column the area of the peaks were taken to be directly proportional to the concentration of the respective isomers because signal area was identical within the range of experimental error. Peak areas were then determined either by the triangulation (peak height × ½ peak width) or the weighing method.

For two peaks partially resolved their ratio was determined by curve-fitting or by Bartlett and Smith's method.[71]

Relative reactivities. The mixtures obtained in the competitive experiments were analysed quantitatively from the combined areas of the peaks representing the isomeric substituted *o*-, *m*-, and *p*-2-phenylthiazoles (ΣA_i) and 2-phenylthiazole (A) after correction for the molecular weights of 2-arylthiazoles (M_i) and 2-phenylthiazole (M). Formula (1) was used.

$$\frac{\text{Ph}}{\text{Ph}}\frac{\text{X}}{\text{H}}k = \frac{\Sigma A_i}{A} \times \frac{M}{M_i} \qquad (1)$$

Yield determination. The internal standard method was used.[72] The crude mixture was first analysed by g.l.c. then a known amount of biphenyl (or 4-bromobiphenyl) was added as an internal marker. The mixture was rechromatographed on columns A, B, or C.

To determine the signal area of the 2-phenylthiazole relative to biphenyl, duplicate synthetic mixtures of 2-phenylthiazole and biphenyl were analysed. This value was found to be 1·8 on column A or A′ at 200 °C, close to that for other isomeric phenylthiazoles or phenylisothiazoles.

T.l.c.[73] All reaction mixtures and synthetic compounds were analysed by t.l.c. according to Stahl's procedure.[74] These analyses were carried out on silica and alumina $HF_{254+366}$ with benzene, chloroform, or carbon tetrachloride as eluants, in an unsaturated atmosphere.

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By application of Snyder's theory,[75] chromatographic data for several arylthiazoles have been reported.[76]

Column chromatography. 2-Arylbenzothiazole mixtures were fractionated over silica (15 g) with a 12 × 2 cm (i.d.) column. The mixture (1 g) in 5 cm^3 of methylene dichloride was eluted with the same solvent for aromatic compounds and afterwards a mixture of hexane and methylene dichloride (1 : 1) was used to separate 2-arylbenzothiazoles. Each fraction was again controlled by t.l.c.

N.m.r. All n.m.r. spectra were performed with Varian A-60 or HA 100 MHz spectrophotometers for CCl_4 or $CDCl_3$ as solvent. Quantitative analysis by n.m.r. were carried out on reaction mixtures resulting from the attack of anisole and toluene by thiazol-2-yl radicals. The isomer ratios obtained from n.m.r. and g.l.c. analysis are compared in Table 5.

TABLE 5

Isomer ratios

Compounds	Method	*o*	*m*	*p*	f_m/f_p
Methoxybiphenyl	G.l.c.	60	21·3	18·7	0·57(A′ at 220°)
	N.m.r.	55 [a]	23·5	21·5	0·55
2-Methoxyphenylthiazole	G.l.c.	66·5	33·5	(unresolved)	(A at 220°)
	N.m.r.	65	10	25	0·2

[a] Results obtained by thermal decomposition of benzoyl peroxide in anisole at 140 °C; isomers were isolated by preparative g.l.c.

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