PHOTOLYSIS OF BROMOTHIAZOLES IN HYDROGEN-DONATING SOLVENTS. A THEORETICAL STUDY AND PHYSICAL PROPERTIES OF BROMOTHIAZOLES§

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Abstract - Uv irradiation of bromothiazoles in various organic solvents (methanol, ether, cyclohexane) produces thiazole and the isomeric isothiazole as the main reaction products. The reactivity of monobromothiazoles in this reaction decreases in the order: 2-bromothiazole > 5-bromothiazole >> 4-bromothiazole. The PPP (LCI-SCF-MO) calculations of bromothiazoles were used to interpret and discuss their various properties. The uv, NMR, and mass spectra of bromothiazoles were measured.

INTRODUCTION

In addition to other reaction products, the parent unsubstituted heterocycles are formed in the photolysis of bromothiophenes,[1] bromoquinolines,[2] bromoisoquinolines,[2] and bromopyrimidines[3-5] carried out in solvents viable to hydrogen abstraction. The distribution of the various reaction products and the reaction mechanism vary widely with the experimental conditions (for recent reviews, see refs. 6,7). In contrast to the above-mentioned photodebrominations, bromopyridines and 2-bromoquinoline undergo alkaline photohydrolysis with the formation of the respective hydroxy derivatives or their oxo tautomers.[8,9]

As a continuation of our previous studies,[1,2,6,7,10-14] we wish to report the results obtained in the photolysis of bromothiazoles in hydrogen-donating solvents. The compounds used in the

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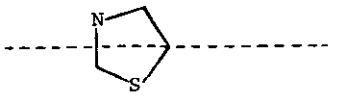
study were 2-bromothiazole, 4-bromothiazole, 5-bromothiazole, 2,4-dibromothiazole, 2,5-dibromothiazole, and 2-bromo-5-phenylthiazole (cf. Scheme 1). PPP (LCI-SCF-MO) calculations have been carried out for the models of these compounds and the results have been used to interpret and to discuss their various physical properties.



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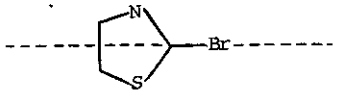
Thiazole



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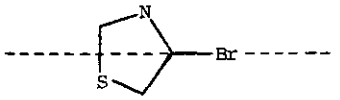
2-Bromothiazole



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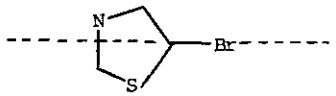
4-Bromothiazole



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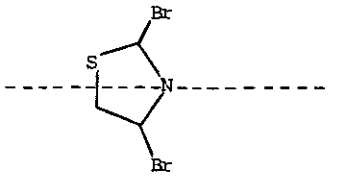
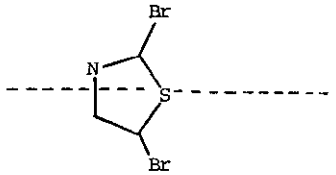
5-Bromothiazole



5
2,4-Dibromothiazole



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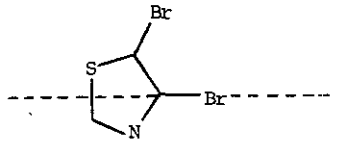
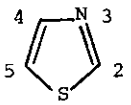
2,5-Dibromothiazole



7
4,5-Dibromothiazole

Numbering:



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Scheme 1

Thiazoles Studied

RESULTS AND DISCUSSION

Electronic Spectra. The electronic absorption spectra of bromothiazoles are summarized in Table 1. The results of PPP calculations (Table 2) predict two allowed transitions in the usual region of

Table 1. Electronic Absorption Spectra of Bromothiazoles[a]

No.	Compound	λmax, nm (ε)
1	Thiazole	208 (~2,600), 233 (~3,700)[b]
2	2-Bromothiazole	211 (3,100), 248 (5,400)
3	4-Bromothiazole	246.5 (2,800)
4	5-Bromothiazole	218 (3,100), 245 (4,400)
5	2,4-Dibromothiazole	213 sh (3,000), 258 (3,900)
6	2,5-Dibromothiazole	222.5 (2,800), 260 (6,900)
8	2-Phenyl-5-bromothiazole	213 (10,000), 298 (16,200)

[a] In ethanol. [b] Ref. 15. Cf. also ref. 16.

Table 2. Calculated Spectral Characteristics of Bromothiazoles[a]

No.	Compound	ΔE^{1}[b] eV	ΔE^{1}[b] kK	f[c]	cos φ[d]	Predominant configuration i,j[e]	Wt	ΔE^{3}[f] eV	ΔE^{3}[f] kK
1	Thiazole	5.131	41.39	0.236	-0.996	1,-1	0.805	2.282	18.41
		5.697	45.96	0.134	-0.617	2,-1	0.645	3.745	30.21
		7.256	58.54	0.811	0.211	1,-2	0.753	4.592	37.04
		7.806	62.97	0.322	-0.985	2,-2	0.953	6.064	48.92
2	2-Bromothiazole	5.124	41.34	0.244	-0.869	1,-1	0.817	2.289	18.46
		5.689	45.90	0.130	0.961	2,-1	0.648	3.746	30.21
		7.245	58.45	0.816	0.403	1,-2	0.747	4.612	37.20
		7.809	63.00	0.318	-0.699	2,-2	0.954	6.060	48.87
3	4-Bromothiazole	5.106	41.19	0.233	0.384	1,-1	0.812	2.275	18.35
		5.702	46.00	0.134	0.937	2,-1	0.652	3.744	30.20
		7.231	58.34	0.812	-0.873	1,-2	0.752	4.587	36.99
		7.808	62.99	0.331	-0.114	2,-2	0.948	6.075	49.00
4	5-Bromothiazole	5.111	41.24	0.245	-0.994	1,-1	0.823	2.285	18.43
		5.691	45.92	0.127	-0.615	2,-1	0.651	3.748	30.23
		7.242	58.42	0.820	-0.266	1,-2	0.750	4.583	36.97
		7.806	62.98	0.315	0.990	2,-2	0.958	6.081	49.05
5	2,4-Dibromothiazole	5.099	41.14	0.241	-0.746	1,-1	0.823	2.282	18.41
		5.694	45.94	0.130	0.041	2,-1	0.654	3.744	30.20
		7.221	58.26	0.818	-0.734	1,-2	0.746	4.606	37.15
		7.811	63.01	0.325	-0.907	2,-2	0.949	6.071	48.97
6	2,5-Dibromothiazole	5.105	41.18	0.253	0.185	1,-1	0.833	2.292	18.49
		5.685	45.87	0.123	0.560	2,-1	0.653	3.747	30.22
		7.231	58.34	0.824	-0.996	1,-2	0.744	4.604	37.13
		7.810	63.01	0.311	-0.437	2,-2	0.959	6.078	49.02
7	4,5-Dibromothiazole	5.087	41.04	0.243	0.401	1,-1	0.829	2.278	18.37
		5.696	45.95	0.127	-0.938	2,-1	0.657	3.747	30.22
		7.217	58.23	0.821	-0.866	-1,-2	0.749	4.578	36.92
		7.808	62.99	0.323	0.143	2,-2	0.953	6.093	49.14

[a] Additional theoretical quantities concerning the models of compounds given in Table 1 can be obtained upon request from the authors (C.P.). [b] Excitation energies (eV) and the corresponding wavenumbers (kK) for the four lowest excited singlet states. [c] Oscillator strength. [d] ϕ is the angle formed by the positive direction of the axis shown in the formula (see Scheme 1) and the direction of the transition moment read counterclockwise. [e] A combination of two figures is used to label a configuration. A positive number refers to an orbital occupied in the ground state, a negative number to a virtual orbital. [f] Excitation energies (eV) and the corresponding wavenumbers (kK) for the four lowest excited triplet states.

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the uv spectrum, with the first transition occurring at about 41 kK and the shorter-wavelength transition between 45 and 46 kK. These transitions are associated with the excitations from the highest occupied to the lowest unoccupied π-molecular orbital and from the second highest occupied to the lowest unoccupied π-molecular orbital, respectively (i.e., 1,-1 and 2,-1 transitions). In agreement with the above prediction, the absorption spectra of thiazole and bromothiazoles possess two broad absorption bands. A comparison of these two bands with the results of the calculations indicates that both of them correspond to $\pi \rightarrow \pi^*$ transitions. There is a good agreement between the experimental longest-wavelength absorption bands corresponding to the $S_0 \rightarrow S_1$ transition and the corresponding calculated values (Table 3). Although the second transition is predicted in the correct region, the quantitative agreement with the experimental absorption bands is much poorer. As an example of a successful correlation, the experimental absorption curve for 4-bromothiazole is compared with the results of the PPP calculations in Fig. 1. According to Depeshko,[17] the longest-wavelength absorption band of thiazole corresponds to an $n \rightarrow \pi^*$ transition. Our results do not support this assumption.

Table 3. Comparison of Calculated and Experimental $S_0 \rightarrow S_1$ ($\pi \rightarrow \pi^*$) Transitions of Monobromothiazoles[a]

No.	Compound	$S_0 \rightarrow S_1$			
		$\tilde{\nu}_{calcd}$, kK	4 + log f	$\tilde{\nu}_{exptl}$, kK	log ε
1	Thiazole	41.39	3.37	42.92	3.57
2	2-Bromothiazole	41.34	3.39	40.32	3.73
3	4-Bromothiazole	41.19	3.37	40.57	3.45
4	5-Bromothiazole	41.24	3.39	40.82	3.64

[a] 4 + log f $\doteq$ log ε.

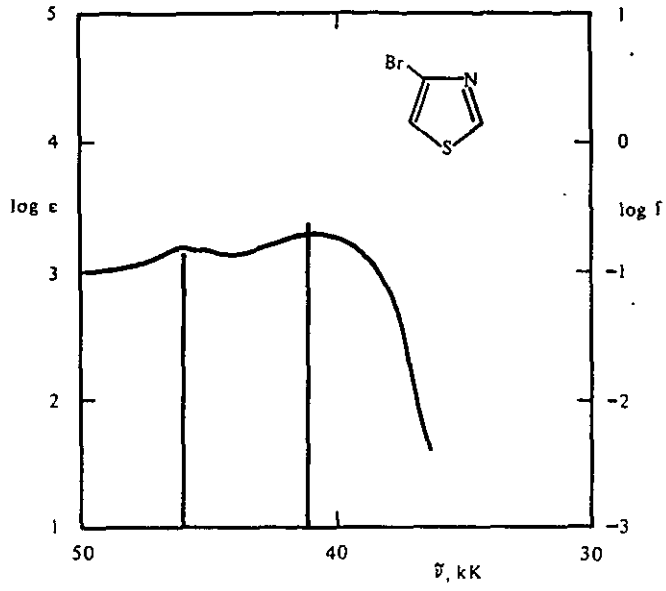


Fig. 1. Electronic absorption spectrum of 4-bromothiazole. Calculated LCI transition energies and intensities are shown as vertical straight lines. Scale for the calculated oscillator strength is shown on the right-hand side.

Almost no emission data could be obtained for bromothiazoles, with the exception of 5-bromothiazole (4) and 2,4-dibromothiazole (5) (Table 4). The experimental $S_0 \rightarrow T_1$ transitions for these compounds are 20.00 and 19.61 kK, respectively, and the corresponding calculated values are 18.43 and 18.41 kK. However, it is well known that the triplet energies calculated by the PPP method are lower than the experimental values unless the parameterization is changed for the triplet states. In all cases, the intensity of the observed emission is very low. These results suggest that in the case of bromothiazoles the photoexcited molecules are deactivated predominantly via radiationless degradation to the ground state which must shorten the lifetime of the respective excited states well below the values of their emission lifetimes.

Table 4. Emission Characteristics of Bromothiazoles[a]

No.	Compound	Fluorescence[b]		Phosphorescence[c]	
		λ_{exc}, nm	λ_{em}, nm	λ_{exc}, nm	λ_{em}, nm
4	5-Bromothiazole	—	—	340	500
5	2,4-Dibromothiazole	340	382	345	510

[a] The bromothiazoles not given in the table give practically no emission. Only weak emission was obtained with the two compounds listed. [b] In ethanol at room temperature. The following additional results were obtained with 2,4-dibromothiazole: methylcyclohexane (room temperature), λ_{exc} 340 nm, λ_{em} 388 nm; EPA (77°K), λ_{exc} 345 nm, λ_{em} 383 nm. [c] In EPA at 77°K.

NMR Spectra. The proton NMR spectra of bromothiazoles are, in general, similar to the NMR spectrum of thiazole itself (Table 5). Thus, the NMR spectral data for bromothiazoles are in accord with their structures.

Table 5. ^{1}H NMR (100 MHz) Spectra of Bromothiazoles[a]

No.	Compound	Solvent	Chemical Shift, δ(ppm) (q_C)[b] H(2)	H(4)	H(5)
1	Thiazole[c]	C_6H_{12}	8.68 (0.953)	7.83 (1.002)	7.19 (1.086)
2	2-Bromothiazole	CCl_4	-	7.50 (1.002)	7.25 (1.088)
3	4-Bromothiazole	CCl_4	8.70 (0.953)	-	7.24 (1.090)
4	5-Bromothiazole	CCl_4	8.65 (0.955)	7.74 (1.006)	-
5	2,4-Dibromothiazole	CCl_4	-	-	7.12 (s) (1.093)
6	2,5-Dibromothiazole	$CDCl_3$	-	7.45 (s) (1.006)	-
8	2-Phenyl-5-bromothiazole[d]	CCl_4	-	7.66 (s)	-

[a] From internal Me_4Si. For the NMR spectrum of thiazole (60 MHz), see refs. 19, 20. [b] The SCF-MO π-electron density on the respective carbon atom. [c] Taken from ref. 19. [d] Chemical shifts in the phenyl ring: o 7.74-7.86 (m), m + p 7.32-7.44 (m).

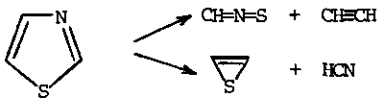
The relationship between the experimental proton chemical shifts and the calculated π-electron densities on the respective carbon atoms (to which the protons are bonded) is well known, although in many cases no satisfactory correlations can be obtained.[18] In the case of bromothiazoles, there is a satisfactory linear relationship between the experimental δ values and the calculated q_C's which can be expressed by a regression line

$$\delta \text{ (ppm)} = -9.87\, q_C + 17.83$$

Number of points n = 11, correlation coefficient r = 0.907.

All data are significant on 1% probability level.

Mass Spectra. The mass spectral data obtained for bromothiazoles are summarized in Table 6. It has been well established that the unsubstituted thiazole fragments upon electron impact by two major routes involving loss of acetylene or hydrogen cyanide.[21,22]



It can be seen (Table 6) that the ions corresponding to the above intermediates are also important in the fragmentation of bromothiazoles.

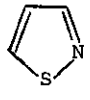
Photolysis. Solutions containing the substrate in methanol, cyclohexane, or ether were irradiated in pyrex vessels, i.e., with λ ~300 nm and longer. This means that the bromothiazoles were irradiated in the longest-wavelength portion of their absorption curve. At shorter wavelengths thiazole, isothiazole, and their derivatives undergo photoisomerization and are easily converted into their respective isomers.[23-25]

Table 6. Mass Spectra of Bromothiazoles, Principal Fragments, and Relative Intensities[a]

No.	Compound	Principal fragments, m/e (rel. intensity, %)
1	Thiazole[b]	87 (5), 86 (5), 85 (100), 60 (3), 59 (4), 58 (70), 57 (9), 45 (7), 44 (4), 42 (2)
2	2-Bromothiazole[c]	165 (8.8), 164 (4), 163 (8.3), 93 (4.8), 91 (4.7), 83 (8.9), 81 (10.3), 79 (11), 60 (9.3), 59 (9), 58 (100), 57 (36), 56 (7), 44 (7)
3	4-Bromothiazole	165 (78), 164 (5), 163 (74), 136 (44.5), 135 (6.5), 134 (44.5), 82 (7.2), 81 (9), 79 (9.3), 59 (7.6), 58 (8.6), 57 (100), 56 (16), 51 (10.3), 45 (46.5), 44 (10)
4	5-Bromothiazole	165 (56), 164 (3), 163 (54.5), 138 (11), 136 (11), 86 (6.5), 85 (7.2), 84 (96.3), 79 (9), 59 (7.8), 58 (9), 57 (100), 56 (15.4), 45 (24.5), 44 (12.6)
5	2,4-Dibromothiazole	245 (53), 243 (100), 241 (52), 168 (8), 149 (26), 138 (35), 137 (10), 136 (35), 135 (10), 125 (12), 123 (12), 93 (10), 91 (10), 83 (22), 82 (33), 81 (20), 80 (26), 79 (18), 76 (12), 71 (10), 70 (9), 69 (10), 67 (8), 60(8), 59 (8), 58 (8), 57 (55), 56 (22), 55 (26), 51 (10), 45 (26), 44 (26), 43 (35)
6	2,-5-Dibromothiazole	245 (47), 243 (100), 241 (49), 163 (5), 162 (95), 161 (5), 160 (90), 138 (10) 136 (10), 125 (5), 106 (5), 104 (5), 93 (7), 91 (8), 84 (5), 83 (44), 82 (17), 81 (12), 79 (7.5), 59 (5), 58 (9), 57 (72), 56 (10), 45 (7.5), 44 (8.5)
7	2-Phenyl-5-bromothiazole	241 (37), 240 (100), 239 (94), 162 (10), 161 (22), 160 (47), 138 (10), 136 (10), 133 (12), 116 (17), 103 (21), 89 (10), 80 (7), 77 (24), 76 (20), 75 (10), 71 (10), 63 (8), 62 (6), 59 (6), 58 (7), 57 (88), 51 (18), 50 (15), 43 (5)

[a] Molecular ions are underlined. [b] Ref. 21. Cf. also 22. [c] Ref. 21 gives 167 (3), 166 (2), 165 (70), 164 (2), 163 (70), 125 (1), 123 (1), 108 (1.5), 106 (1.5), 93 (1), 91 (1), 60 (6), 59 (5), 58 (100), 57 (12), 56 (2), 45 (7), 44 (5), 40 (2), 38 (2).

Uv irradiation of the bromothiazoles gives thiazole (1) and its isomer isothiazole (9) as the principal reaction products. Isothiazole is formed by the photoisomerization of thiazole. The rate of photodebromination decreases in the order: 2-bromothiazole (30% yield) > 5-bromothiazole (15-20%) >> 4-bromothiazole (0.5%). Providing that, under comparable conditions, the reaction mechanism is



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identical for all isomers, the quantum yields can be expected to decrease in the same order as the chemical yields. Although the quantum yields in this reaction were not determined, they should not be too different from those obtained with bromothiophenes[1] (ϕ ~0.04-0.10) and bromoquinolines and -isoquinolines[2] (ϕ ~0.02-0.07). In the case of 2,4-dibromothiazole, the main reaction product is 4-bromothiazole, along with traces of thiazole. Uv irradiation of 2,5-bromothiazole gives slightly larger amounts of thiazole and isothiazole, 5-bromothiazole, as well as 4-bromothiazole formed by the photoisomerization of the latter compound.

No changes in the composition of the reaction products were observed with iodine added to the solutions of the substrates in cyclohexane or ether, and oxygen does not exhibit any noticeable effect upon the reaction. On the other hand, triethylamine accelerates the photodebromination rate and its effect decreases in the order 5-bromothiazole > 2-bromothiazole >> 4-bromothiazole. Photolysis of 5-bromothiazole in methanol gives traces of a product with mol. wt. of 194-196 which could be 2-hydroxymethyl-5-bromothiazole or the corresponding dihydro derivative. The formation of such a hydroxymethyl derivative can be explained as the result of a homolytic cleavage of a C-H bond in the methyl group of methanol and the subsequent recombination of the hydrogen atom combines with the thiazolyl radical to give thiazole. A hydroxymethyl radical is then another species formed in the process and available in the reaction mixture.[2] We have shown that in reactions of this type the abstraction of hydrogen from methanol occurs from the methyl group and not from the hydroxy group.[2] No bithiazoles were detected in the reaction mixture which would be formed by coupling of two thiazolyl radicals.

On the basis of the experimental results obtained, it seems that the reaction mechanism in hydrogen-donating solvents is similar to that observed with bromothiophenes,[1] involving homolytic cleavage of the C-Br bond and perhaps the formation of a π-complex between the bromine atom and the respective thiazolyl radical, followed by abstraction of hydrogen from the solvent leading to thiazole. It is likely that in the presence of an amine the mechanism involves electron transfer with the formation of an exciplex. The bromothiazole radical anion then undergoes a cleavage of the C-Br bond with the formation of the bromide anion and thiazolyl radical which reacts with the solvent and gives thiazole.[2]

The first excited singlet state is probably the state undergoing the reaction (there is no or very weak phosphoresence from bromothiazoles). It is likely that the differences in the reactivity of the isomeric bromothiazoles are caused by the differences in the C-Br bond strengths. In ground-state bromothiazoles, such differences in the C-Br bond strengths can be inferred from the relative abundances of ions obtained by a loss of bromine from the molecular ion in the mass spectra of bromothiazoles (Table 6). Such values are not readily available for the excited states.

EXPERIMENTAL

PPP(LCI-SCF-MO) Treatment. The usual version of the PPP method was used.[26] Interactions between all monoexcited configurations formed by promotion of one electron from one of the occupied MO's to one of the vacant MO's were considered. No participation of the d orbitals of sulfur was considered. The systems studied were assumed to be planar and to have idealized geometry. All C-C, C-N, and C-S bond lengths were assumed to be 1.40 A and the C-Br bond length was taken as 1.86 A. The rings were assumed to be regular pentagons. SCF MO's served as the basis for CI calculations. Only resonance integrals between nearest neighbors were considered. The parameters used in the calculations are summarized in Table 7.[27] The results of the calculations are shown in Table 2.

Table 7. Parameters Used in the PPP Calculations[a]

Atom, μ	I_μ	A_μ	$\lambda_{\mu\mu}$	Z_μ	$\beta_{C-\mu}$
C	11.22	0.69	10.53	1	-2.318
N	14.10	1.80	12.30	1	-2.318
S	20.27	10.47	9.80	2	-1.623
Br	22.07	14.50	7.57	2	-0.695

[a] Values in eV. I_μ and A_μ are the ionization potential and the electron affinity of the atom μ in the atomic valence state, respectively. The monocentric electronic repulsion integrals and resonance integrals between nearest neighbors are represented by $\lambda_{\mu\mu}$ and $\beta_{C-\mu}$, respectively. Z_μ is the core charge at atom μ.

The bicentric electronic repulsion integrals were calculated using the Mataga-Nishimoto formula:[28]

$$\gamma_{\mu\nu} = \frac{14.399}{l_{\mu\nu} + 1.328} \quad \text{eV}$$

where $l_{\mu\nu}$ (in A = 10^{-1} nm) is the distance between atoms μ and ν. The calculations were carried out on an IBM 360/65 computer.

Materials. 2-Bromothiazole, 4-bromothiazole, 5-bromothiazole, 2,4-dibromothiazole, 2,5-dibromothiazole, and 2-phenyl-5-bromothiazole were synthesized using procedures described in the literature. The yields of the bromothiazoles obtained and their melting or boiling points are summarized in Table 8. All melting and boiling points are uncorrected.

Table 8. Yields and Physical Characteristics of Bromothiazoles

No.	Compound	% Yield (isolated)	M.p., °C (Lit.)	B.p., °C/mm (Lit.)	Ref.
2	2-Bromothiazole	90	-	54/9 (171-174/760)	29,30
3	4-Bromothiazole	51.5	-	72/20 (189-190/760)	31
4	5-Bromothiazole	36	-	45/7 (62-63/15, 81/18)	30,32
5	2,4-Dibromothiazole	64	80-82 (82)	-	33
6	2,5-Dibromothiazole	23	46 (45-47)	-	33,
8	2-Phenyl-5-bromothiazole	10	78-80	-	35

Electronic Spectra. Uv absorption spectra were recorded on Cary 14 and Beckman Acta V spectrophotometers in ethanol solutions using 1 cm quartz cells and are presented in Table 1. The emission measurements were carried out with an Aminco-Bowman spectrophotofluorometer equipped with the Aminco-Keirs phosphoroscope accessory. The fluorescence experiments were performed at room temperature in ethanol and methylcyclohexane, the phosphorescence was studied in EPA at 77°K. The available information on their emission spectra is given in Table 4.

NMR Spectra. NMR spectra were obtained on a Varian HA-100 spectrometer in carbon tetrachloride or deuterochloroform, with tetramethylsilane as the internal standard. A summary of the recorded data is given in Table 5.

Mass Spectra. Mass spectra were taken on an AEI Model MS 9 spectrometer operating at 70 eV ionizing potential. The principal fragments and relative intensities are presented in Table 6.

Irradiations. Iradiations were carried out at room temperature in pyrex vessels using a water-cooled Hanau PQ 150 W high-pressure mercury lamp. All samples were irradiated for 24 hr. The concentration of the solutions was 0.5-1.0 mmole of the substrate in 300 ml of methanol. Some irradiations were performed in ether or cyclohexane as the solvent. The irradiations were carried out both in the presence of oxygen and under nitrogen, with various substances added in certain runs (iodine, triethylamine, water, hydrochloric acid, sodium hydroxide). After the reaction, 2 ml of concentrated hydrochloric acid were added to convert the thiazole and isothiazole formed into their respective hydrochlorides. The solvent was evaporated on a rotary evaporator, the residue was neutralized with sodium carbonate, and extracted with ether. The ether solution was then dried and evaporated. The residue after evaporation was analyzed by the usual techniques (GC, TLC, GC-MS).

Analytical Methods. Details of the analytical conditions are as follows. GC. The products were analyzed by gas chromatography using an Intersmat IGC 15 gas chromatograph equipped with a flame ionization detector and coupled with a Vidar Autolab integrator. The following three stainless 8-in. columns were used: A was a 5-ft column packed with Carbowax 20 M (10%) on Chromosorb Q (80-100 mesh). B was a 7-ft column packed with Apiezon L (10%) on Chromosorb W, HMDS (80-100 mesh). C was a 7-ft column packed with Silicone SE-30 (10%) on Chromosorb W, HMDS (60-80 mesh). Also a column packed with OV 225 was used. The Kováts indices obtained for various bromo-substituted thiazoles are shown in Table 9.

Table 9. Kováts Indices, I, of Bromothiazoles[a]

No.	Compound[b]	I Column[c] (Temp., °C) A (125)	B (120)	C (185)
1	Thiazole	1260	760	720
2	2-Bromothiazole	1530	1000	1030
3	4-Bromothiazole	1690	1150	-
4	5-Bromothiazole	1650	1130	-
5	2,4-Dibromothiazole	1535	1070	-
6	2,5-Dibromothiazole	1530	1030	-
-	2-Chloro-4-bromothiazole	1800	1265	-
-	2-Chloro-5-bromothiazole	1750	1240	-

[a] Kováts indices were calculated according to the general formula[37] $I = 200\,[\log(d'_R)_X - \log(d'_R)_Z]/[\log(d'_R)_{Z+2} - \log(d'_R)_Z] + 100\,Z$ where d'_R represents the reduced retention distance. [b] All halo-substituted thiazoles were obtained using procedures reported in the literature. [c] For the description of the columns, see text.

GC-MS. These analyses were performed using Aerograph Model 1400 and Varian MAT 111 instruments at 80 eV. The column used was 5 ft x 0.125 in. OV 225 (5%) on Varaport (100-120 mesh), operated in programmed temperature range 100-250°C, 4-6°C min^{-1}.

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