Photochemical Synthesis of 2-Substituted Benzothiazoles

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The photochemical reaction of 1-indolethiocarbanilides **1**, di- and tri-substituted thioureas **3-5** and 4,4-dimethyl-2,6-dioxothiocyclohexanecarboxanilides **9** affording the respective benzothiazoles are described.

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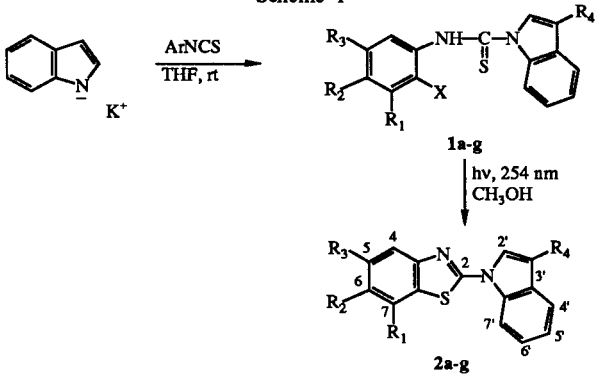
We have earlier reported [1,2] the formation of the benzothiazole ring system by the irradiation of *o*-halothioacetanilides. An extension of this method has given rise to the synthesis of naphtho[1,2-*d*]thiazoles and naphtho[2,1-*d*]thiazoles [3]. We present here the general applicability of the facile photocyclization for the synthesis of new derivatives of benzothiazoles with a variety of substituents at the 2-position, eg, 2-(indol-1-yl), 2-anilino, 2-diphenylamino, 2-(dimedon-2-yl).

By following a reported procedure [4], the indolyl potassium was prepared in THF and treated with aryl isothiocyanates [5] at room temperature for 15 hours to obtain the respective 1-indolethiocarbanilides **1a-g** in 75-85% yields. The irradiation of the thiocarbanilide was carried out at 254 nm using Rayonet photochemical reactor in methanol solution and the product purified by column chromatography to isolate the respective 2-(indol-1-yl)benzothiazoles **2a-g** in moderate to high yields (Scheme 1). The same reaction when carried out in benzene medium, also yielded the product with the same efficiency and characterised by ir, ^{1}H-nmr, ms and microanalytical data.

The unsubstituted 1-indolethiocarbanilide remained unaffected under irradiation conditions without or with a catalytic amount of iodine.

Scheme 1

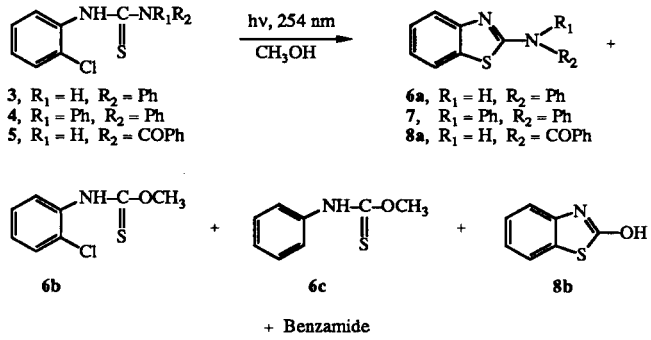


1,2	X	R_1	R_2	R_3	R_4
a	Cl	H	H	H	H
b	Br	H	H	H	H
c	Cl	Cl	H	H	H
d	Cl	H	H	Cl	H
e	Br	H	CH_3	H	H
f	Cl	–CH=CH–CH=CH–		H	H
g	Cl	H	H	H	CH_3

N-(2-Chlorophenyl)-*N'*-phenylthiourea (**3**), prepared from aniline and *o*-chlorophenyl isothiocyanate, was irradiated at 254 nm in chloroform-methanol (2:15) solution until all the starting material disappeared (tlc). The reaction mixture on chromatographic separation over silica gel afforded three products identified by ir, ^{1}H-nmr, mass spectral data as 2-anilinobenzothiazole [6] (**6a**, 18%), *o*-chlorophenylthiocarbamic acid *O*-methyl ester [7] (**6b**, 25%) and phenylthiocarbamic acid *O*-methyl ester [7] (**6c**, 22%). Authentic samples of **6b** and **6c** were prepared from the reaction of respective isothiocyanate with potassium hydroxide in methanol and compared with the photoproducts (Scheme 2).

N'-(2-Chlorophenyl)-*N*,*N*-diphenylthiourea **4**, prepared from *o*-chlorophenyl isothiocyanate and diphenylamine, was irradiated at 254 nm in methanol for 21 hours. The 2-(*N*,*N*-diphenylamino)benzothiazole **7** was isolated in 49% yield after chromatographic separation over silica gel.

Scheme 2



The *N*-benzoyl-*N'*-(*o*-chlorophenyl)thiourea [8] **5** on irradiation in methanol for 65 hours at 254 nm furnished the following four products separated by chromatography: (i) 2-benzoylaminobenzothiazole [9] **8a** (14%) (ii) 2-hydroxybenzothiazole [6] **8b** (19%) (iii) benzamide (36%) and (iv) **6b** (26%). The cleavage of the thiourea was noticed if it is disubstituted (**3** and **5**) but not trisubstituted (**4**) resulting in the products **6b** and **6c** from **3** and **6b** and benzamide from **5**. The thiocarbamate **6b** on further photolysis afforded the 2-hydroxybenzothiazole **8b**. Also it was observed that the 2-benzoylaminobenzothiazole **8a** was unaffected by methanol with or without added dilute

Table 1
Physical and Analytical Data of Compounds **1a-g, 2a-g, 4,7, 9a-c, 10a-c**

Compound No.	Irradiation time (hours)	Yield (%)	Mp (°C) (solvent)	Molecular Formula (mole weight)	Analysis (%) Calcd./Found C	H	N
1a	–	82	113-115 (EtOH)	$C_{15}H_{11}ClN_2S$ (286.8)	62.82 62.91	3.87 3.83	9.77 9.70
1b	–	76	100-102 (EtOH)	$C_{15}H_{11}BrN_2S$ (331.2)	54.39 54.10	3.35 3.25	8.46 8.57
1c	–	86	129-131 (EtOH)	$C_{15}H_{10}Cl_2N_2S$ (321.2)	56.09 55.80	3.14 3.20	8.72
1d	–	73	90-92 (EtOH)	$C_{15}H_{10}Cl_2N_2S$ (321.2)	56.09 55.88	3.14 3.04	8.72 8.64
1e	–	74	120-122 (EtOH)	$C_{16}H_{13}BrN_2S$ (345.3)	55.66 55.57	3.80 3.74	8.11 8.19
1f	–	86	154-156 (EtOH)	$C_{19}H_{13}ClN_2S$ (336.8)	67.75 67.89	3.89 3.82	8.32 8.21
1g	–	53	141-143 (EtOH)	$C_{16}H_{13}ClN_2S$ (300.8)	63.89 63.70	4.36 4.31	9.31 9.16
2a (= 2b) [a]	55	34	110-112 (B/P)	$C_{15}H_{10}N_2S$ (250.3)	71.97 72.10	4.03 4.01	11.19 11.20
2c	35	47	125-127 (B/P)	$C_{15}H_9ClN_2S$ (284.8)	63.27 63.40	3.19 3.10	9.84
2d	20	73	120-122 (B/P)	$C_{15}H_9ClN_2S$ (284.8)	63.27 63.19	3.19 3.08	9.84 9.63
2e	28	57	98-100 (B/P)	$C_{16}H_{12}N_2S$ (264.4)	72.70 72.52	4.58 4.67	10.60 10.51
2f	8	85	146-148 (B/P)	$C_{19}H_{12}N_2S$ (300.4)	75.97 76.23	4.03 3.96	9.33 9.18
2g	42	32	116-118 (B/P)	$C_{16}H_{12}N_2S$ (264.4)	72.70 72.70	4.58 4.44	10.60 10.37
4	–	35	138-140 (Benzene)	$C_{19}H_{15}ClN_2S$ (338.9)	67.35 67.25	4.46 4.44	8.27 7.92
7	21	49	108-110 (B/P)	$C_{19}H_{14}N_2S$ (302.4)	75.47 75.56	4.67 4.64	9.26 9.01
9a	–	91	144-145 (B/P)	$C_{15}H_{16}ClNO_2S$ (309.8)	58.15 57.99	5.21 5.27	4.52 4.45
9b	–	89	144-146 (B/P)	$C_{16}H_{18}BrNO_2S$ (368.3)	52.18 52.22	4.93 4.97	3.80 3.43
9c	–	79	167-169 (B/P)	$C_{19}H_{18}ClNO_2S$ (359.9)	63.41 63.03	5.04 4.97	3.89 3.66
10a	55	56	204-205 (Lit [10] 203-203.5°)	$C_{15}H_{15}NO_2S$ (273.4)			
10b	45	83	221-223 (Lit [10] 225-226°)	$C_{16}H_{17}NO_2S$ (287.4)			
10c	30	47	221-223 ($CHCl_3$)	$C_{19}H_{17}NO_2S$ (323.4)	70.56 70.20	5.30 5.20	4.33

[a] Compound **2b** (from **1b**), time: 22 hours, Yield: 45%.

hydrochloric acid at room temperature or on irradiation (methanol + hydrochloric acid) simulating the photolytic condition wherein the reaction mixture is usually acidic due to the liberated hydrochloric acid during the irradiation. Here the cyclisation was observed; in addition to that, the starting material cleavage also occurred.

The thioamides **9a-c** were prepared from the respective aryl isothiocyanates and dimedone by refluxing in benzene in the presence of triethylamine. The irradiation of thioamide **9a** in methanol at 254 nm for 55 hours afforded 2-(benzothiazol-2'-yl)-5,5-dimethyl-1,3-cyclohexanedione [10] (**10a**) in 56% yield (Scheme 3). Likewise

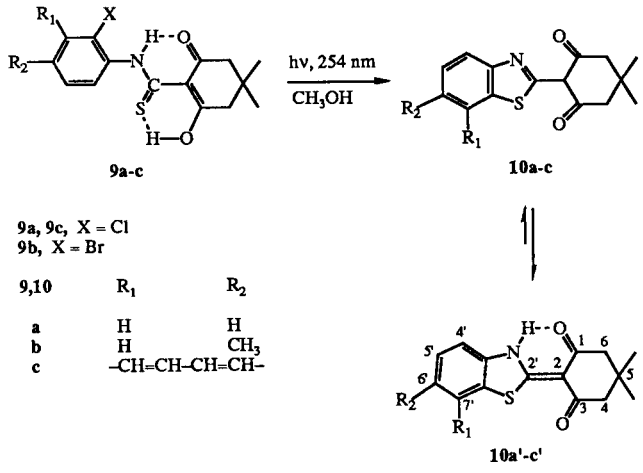
Table 2

Spectral Data of Comounds **1a-g, 2a-g, 4,7, 9a-c, 10a-c**

Compound No.	IR (KBr) (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ	MS (70 eV) m/z (%)
1a	3110, 1470, 1435, 1305, 1185	6.40-6.50 (d, 1H, indole-3H), 7.00-8.16 (m, 9H, ArH), 8.60 (br s, 1H, NH)	286 (M^+, 1), 251, 169, 134, 117(100)
1b	3120, 1485, 1445, 1315, 1190	6.50-6.56 (d, 1H, indole-3H), 6.83-8.10 (m, 9H, ArH), 8.60 (br s, 1H, NH)	–
1c	3190, 1505, 1440, 1345, 1305, 1250	6.53-6.60 (d, 1H, indole-3H), 7.10-8.10 (m, 8H, ArH), 8.60 (br s, 1H, NH)	286 (M^+ -Cl +H, 54), 203, 168, 177 (100)
1d	3210, 1495, 1445, 1345, 1310, 1180	6.70-6.80 (d, 1H, indole-3H), 7.16-8.15 (m, 8H, ArH), 8.83 (br s, 1H, NH)	320 (M^+, 1), 285 (100), 203, 168, 133, 117
1e	3330, 1440, 1350, 1310, 1185	2.30 (s, 3H, CH_3), 6.30-6.40 (d, 1H, indole-3H), 6.73-7.83 (m, 8H, ArH), 8.30 (br s, 1H, NH)	265 (M^+ -Br, 97), 264 (100), 148, 117
1f	3220, 1500, 1450, 1310, 1250	6.20-6.30 (d, 1H, indole-3H), 6.76-7.93 (m, 11H, ArH), 8.50 (br s, 1H, NH)	302 (M^+ -Cl +H, 100), 219, 151, 140, 126, 117
1g	3110, 1490, 1450, 1340, 1320, 1210	2.56 (s, 3H, CH_3), 7.20-8.33 (m, 9H, ArH), 8.65 (br s, 1H, NH)	300 (M^+,2), 265, 169, 134, 130 (100)
2a = 2b	1520, 1430, 1440, 1350, 1200	6.66-6.70 (d, 1H, indole-3H), 7.16-7.96 (m, 8H, ArH), 8.53-8.63 (d, 1H, indole-2H)	250 (M^+, 100), 249, 218, 125 (M^{++}), 142, 89
2c	1520, 1435, 1335, 1195	6.43-6.50 (d, 1H, indole-3H), 6.96-7.56 (m, 7H, ArH), 8.16-8.30 (d, 1H, indole-2H)	285 (M^+ +H, 100), 249, 248, 142, 89
2d	1530, 1510, 1445, 1345	6.96-7.06 (d, 1H, indole-3H), 7.43-8.23 (m, 7H, ArH), 8.70-8.83 (d, 1H, indole-2H)	284 (M^+, 100), 249, 248, 142, 89
2e	1540, 1445, 1340, 1200	2.36 (s, 3H, CH_3), 6.53-6.60 (d, 1H, indole-3H), 7.03-7.76 (m, 7H, ArH), 8.40-8.53 (d, 1H, indole-2H), ^{13}C-nmr ($CDCl_3$): δ = 21.5 (q, Arom-CH_3), 108.0 (d, C-3'), 114.4 (d, C-7), 121.0, 121.3, 121.7, 122.8, 124.4, 126.5, 128.1, 130.5, 131.8, 134.4, 135.6, 149.3 (s, C-3'a), 158.1 (s, C-2)	265 (M^+ +H, 100), 264, 148, 142, 132 (M^{++}), 89
2f	1535, 1440, 1345, 1200	6.30-6.40 (d, 1H, indole-3H), 6.83-7.73 (m, 10H, ArH), 8.23-8.36 (d, 1H, indole-2H)	301 (M^+, +H, 100), 158, 150 (M^{++}), 140, 137
2g	1580, 1520, 1440, 1355	2.40 (s, 3H, CH_3), 7.23-8.03 (m, 8H, ArH), 8.53-8.70 (d, 1H, indole-2H)	264 (M^+, 100), 263, 132 (M^{++}), 130, 119
4	3340, 1485, 1340, 1315	7.02-7.68 (m, 14H, ArH), 7.86 (br s, 1H, NH)	338 (M^+)
7	1520, 1500, 1460, 1450, 1335	6.76-7.50 (m)	302 (M^+, 37), 301, 269, 167 (100), 151 (M^{++}), 140, 139
9a	3420 (b), 2950, 1630, 1515, 1410	1.16 (s, 6H, $(CH_3)C$), 2.57 (s, 2H, CH_2), 2.70 (s, 2H, CH_2), 7.26-7.90 (m, 4H, ArH), 13.73 (br s, 1H, NH), 17.50 (s, 1H, OH)	
9b	3440 (b), 2960, 1620, 1495, 1400	1.16 (s, 6H, $(CH_3)_2C$), 2.40 (s, 3H, Aro-CH_3), 2.53 (s, 2H, CH_2), 2.68 (s, 2H, CH_2), 7.13-7.35 (m, 1H, ArH), 7.46-7.63 (m, 2H, ArH), 13.10 (br s, 1H,NH), 16.95 (s, 1H, OH), ^{13}C-nmr ($CDCl_3$): δ = 21.0 (q, Arom-CH_3), 28.1 (q, $C(CH)_3)_2$) 30.2 (s, C-4), 46.9 (t, CH_2), 52.5 (t, CH_2), 108.2 (s, C-1), 120.2 (s, C-2'), 128.5 (d), 128.6 (d), 133.6 (d), 134.1 (s), 139.3 (s), 190.4 (s, C=S), 191.4 (s, C=O), 199.1 (s, C=O)	288 (M^+ -Br, 26), 287 (100), 244, 231, 218, 203, 190, 189
9c	3420 (b), 2940, 1625, 1500, 1420	1.16 (s, 6H, $(CH_3)_2C$), 2.53 (s, 2H, CH_2), 2.66 (s, 2H, CH_2), 7.53-8.46 (m, 6H, ArH), 13.9 (br s, 1H, NH), 16.96 (s, 1H, OH)	360 (M^+ +H, 11), 324 (100), 323, 226, 177
10a	3420, 2970, 1610, 1560, 1500, 1370	1.20 (s, 6H, $(CH_3)_2C$), 2.55 (s, 2H, CH_2), 2.52 (s, 2H, CH_2), 7.35-7.90 (m, 4H, ArH), 14.60 (br s, 1H, NH), ^{13}C-nmr ($CDCl_3$): δ = 28.6 (q, $C(CH)_3)_2$), 31.5 (s, C-5), 50.2 (t, CH_2), 50.8 (t, CH_2), 104.9 (s, C-2), 114.1 (d, C-4'), 122.4 (d), 124.7 (d), 127.4 (d), 128.5 (s, C-7'a), 137.8 (s, C-3'a), 166.2 (s, C-2'), 193.9 (s, C=O), 195.3 (s, C=O)	273 (M^+, 100)
10b	3440, 2960, 1615, 1555, 1505, 1370	1.13 (s, 6H, $(CH_3)_2C$), 2.46 (s, 3H, Aro-CH_3), 2.51 (s, 4H, $2CH_2$), 7.13-7.50 (m, 3H, ArH), 14.56 (br s, 1H, NH), ^{13}C-nmr ($CDCl_3$): δ = 21.3 (q, Arom-CH_3), 28.5 (q, $C(CH)_3)_2$), 31.4 (s, C-5), 50.5 (t, C-4, 6), 104.7 (s, C-2), 113.8 (t, C-4'), 122.2 (d), 128.6 (s, d), 134.9 (s), 135.7 (s), 165.8 (s, C-2'), 194.4 (s, C-1, 3)	288 (M^+ +H, 100), 236, 232, 190
10c	3440, 2960, 1620, 1560, 1495, 1380	1.3 (s, 6H, $(CH_3)_2C$), 2.62 (s, 2H, CH_2), 2.65 (s, 2H, CH_2), 7.40-8.10 (m, 6H, ArH), 15.15 (br s, 1H, NH)	323 (M^+, 90), 239, 226, 225, 210, 196, 41 (100)

5,5-dimethyl-2-(6′-methylbenzothiazol-2′-yl)-1,3-cyclohexanedione (**10b**) and 5,5-dimethyl-2-(naphtho[2,1-*d*]-thiazole-2′-yl)-1,3-cyclohexanedione (**10c**) were obtained from the thioamides **9b** and **9c** with 83% and 47% respectively.

Scheme 3



The proton magnetic resonance spectra of the amides **9a-c** indicate that the compounds are enolic and that the enolic and the amino hydrogens are involved in strong hydrogen bonding as evidenced by the large downfield chemical shifts of these protons: the enolic proton at δ = 16.95-17.50 ppm and amino hydrogens at δ = 13.10-13.90 ppm. The two methylene protons of the dimedone moiety came as singlets with the difference of 0.13 ppm. In the benzothiazoles **10a-c** the disappearance of the enolic proton and the appearance of only the amino hydrogen was observed; also the chemical shift of the two methylene protons coming closer ($\Delta\delta$ = 0 to 0.03) shows the symmetric nature of the dimedone ring. Hence **10a-c** could be better represented as **10a′-c′**. This observation is in line with earlier reports on the nmr of dimedone derivatives [11]. The ^{13}C-nmr data of **9b**, **10a** and **10b** also support the above inference (see Table). It is noteworthy that the dimedone moiety has remained intact on irradiation to a greater extent than the reported cleavage of the ring leading to a lactone [12].

EXPERIMENTAL

All melting points were uncorrected. The ir spectra were recorded on a Perkin-Elmer 598 spectrophotometer. The ^{1}H-nmr spectra were measured with a Varian EM 390 using TMS as the internal standard and the ^{13}C were recorded on a JEOL FX90Q spectrometer. Mass spectra were recorded on a Hewlett Packard 5985 and Shimadzu QP 1000A spectrometer. The photochemical reactions were carried out in a quartz vessel in a Rayonet RPR-208 reactor and Applied Photo-Physics reactor with low pressure mercury lamps.

Preparation of 1-Indolethiocarbanilides **1a-g**. General Procedure.

A solution of indole (11.7 g, 0.1 mole) in tetrahydrofuran (100 ml) was stirred at reflux with potassium (3.9 g, 0.1 g-atom) until all the metal reacted. To the resulting indolyl potassium, diluted with tetrahydrofuran (100 ml) and cooled to room temperature, was added a solution of the respective phenyl isothiocyanate (0.1 mole) in tetrahydrofuran (100 ml) dropwise over half an hour. The reaction mixture was stirred at room temperature for 15 hours, the solvent removed by distillation under reduced pressure, and the residue dissolved in water (220 ml). The resulting solution was washed with ether (2 × 50 ml) to remove the unreacted isothiocyanate and acidified with dilute hydrochloric acid to yield crude 1-indolethiocarbanilides **1a-g** [see Table] which was recrystallised from ethanol.

Photolysis of 1-Indolethiocarbanilides **1a-g**. General Procedure.

The 1-indolethiocarbanilide, **1a-g**, (5 mmoles) was dissolved in methanol (250 ml) and purged with nitrogen for half an hour. The solution was irradiated in a quartz vessel at room temperature using a Rayonet photoreactor model RPR-208 with low pressure mercury lamps (6 instead of 8) of wavelength 254 nm until the disappearance of the starting material (by tlc). After removal of the solvent *in vacuo*, the product, **2a-g** was separated by column chromatography over silica gel (100-200 mesh) and purified by recrystallisation from benzene/petroleum ether (40-60°).

Photolysis of Thioureas **3-5**.

A solution of *N*-(2-chlorophenyl)-*N*′-phenylthiourea **3** (1.0 g, 3.81 mmoles), [prepared (yield, 81%, mp 170-171°), from aniline and *o*-chlorophenyl isothiocyanate] in dry chloroform (20 ml) and methanol (150 ml) was irradiated through a quartz filter using a Rayonet photoreactor for 45 hours at 254 nm. The solvent was removed under reduced pressure and the residue chromatographed over silica gel to isolate the following three products **6a-c**.

2-Anilinobenzothiazole **6a**.

This compound was obtained in a yield of 18% (150 mg) mp 157-159° (lit [6] mp 159°); ms: m/z 226 (M^+, 68.5), 225 (M^+ -H, 100); ^{1}H-nmr (deuteriochloroform): δ = 7.13-7.70 (m); ir (potassium bromide): ν = 3160, 3100, 3020, 2920, 1610, 1550, 1450 cm^{-1}.

o-Chlorophenylthiocarbamic Acid *O*-Methyl Ester **6b**.

This compound was obtained in a yield of 25% (190 mg) mp 74-76° (lit [7] mp 76°); ^{1}H-nmr (carbon tetrachloride/TMS): δ 4.03 (s, 3H, OCH_3), 6.93-7.30 (m, 4H, ArH), 8.1 (br s, 1H, NH); ir (potassium bromide): ν = 3220 (NH), 1310 cm^{-1}.

Phenylthiocarbamic Acid *O*-Methyl Ester **6c**.

This compound was obtained in 22% of (140 mg) mp 91-93° (lit [7] mp 93.5°); ^{1}H-nmr (carbon tetrachloride/TMS): δ 4.13 (s, 3H, OCH_3), 7.16-7.50 (m, 5H, ArH), 9.36 (br s, 1H, NH); ir (potassium bromide): ν = 3170 (NH), 1370, 1210 cm^{-1}.

N′-(2-Chlorophenyl)-*N*,*N*-diphenylthiourea **4** (550 mg, 1.63 mmoles) (prepared from diphenylamine and *o*-chlorophenyl isothiocyanate, similar to the preparation of **1a-g**) was irradiated in methanol (250 ml) in a Rayonet photoreactor for 21 hours at 254 nm. After removal of the solvent under reduced pressure, the

residue was purified by column chromatography over silica gel and purified by recrystallisation from benzene/petroleum ether (40-60°) to isolate **7** in 49% yield.

A solution of *N*-benzoyl-*N'*-(*o*-chlorophenyl)thiourea **5**, [prepared [8] from benzoyl isothiocyanate and *o*-chloroaniline] (1.0 g, 3.45 mmoles) in methanol (170 ml) was purged with nitrogen and irradiated for 65 hours at 254 nm. The reaction mixture was concentrated under reduced pressure and chromatographed to isolate four products:

2-Benzoylaminobenzothiazole **8a**.

This compound was obtained in 14% (120 mg) mp 188-190° (lit [9] mp 186°); ms: m/z 254 (M^+, 16.5), 105 (100).

2-Hydroxybenzothiazole **8b**.

This compound was obtained in 19% (100 mg) mp 134-136° (lit [6] mp 136°); ms: m/z 151 (M^+, 100), 123, 96.

Benzamide.

This compound was obtained in a yield of 36% (150 mg), (compared with the authentic sample).

o-Chlorophenylthiocarbamic Acid-*O*-Methyl Ester **6b**.

This compound was obtained in a yield of 26% (180 mg).

Preparation of Thioamides **9a-c**.

A solution of dimedone (5.0 g, 36 mmoles) and 2-chlorophenyl isothiocyanate (6.4 g, 38 mmoles) in dry benzene (200 ml) containing triethylamine (5 ml) was refluxed for 21 hours. When all the dimedone has disappeared (tlc), the reaction mixture was concentrated and chromatographed over a column of silica gel and eluted with benzene-petroleum ether (1:1) to isolate **9a** as light yellow crystals, yield 10.0 g (91%), mp 144-145° (benzene-petroleum ether).

Compounds **9b** and **9c** were prepared in the similar way.

Photolysis of Thioamide **9** to **10**.

A methanolic solution (150 ml) of thioamide **9a** (1.5 g, 4.85 mmoles) was purged with nitrogen for half an hour and irradiated at 254 nm for 55 hours. The reaction mixture on concentration and chromatographic purification gave 2-(benzothiazol-2'-yl)-5,5-dimethyl-1,3-cyclohexanedione (**10a**) as a colourless solid, yield 740 mg (56%) (see Table).

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