PHOTOCHEMICAL TRANSFORMATION OF TRITHIOBARBITURATE INTO THIOHYDANTOIN AND IMIDAZOLINOTHIOPHENE DERIVATIVES[1]

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Abstract- Upon irradiation of trithiobarbiturate (**1**), ring contraction reaction occurred to give thiohydantoin (**2** or **3**) and imidazolinothiophene (**4**) derivatives. Further, on treating with iodine, the thiohydantoins (**2** and **3**) undergo ring closure, giving imidazolinothiophene derivatives (**4**).

Although the photochemistry of barbiturates has been studied,[2] little is known about that of their sulfur analogs (thiobarbiturate).[3] Their photochemical behaviors are also of interest in relation to that of extensively investigated thioimides[4] or thioamides,[5] since thiobarbiturate possesses a chromophore which consists of a combination of a thioimide with an amide or a thioamide. In a previous paper, we showed that 1,3,5,5-tetramethyl-2-monothio-, 2,4-dithio-, and 2,4,6-trithiobarbiturates undergo efficient [2+2] photocycloaddition (Paterno-Büchi reaction) with alkenes to give thietanes and/or products arose from fission of the thietane ring as well as cyclic thioimide systems.[6] Interestingly, in the reaction of 1,3,5,5-tetramethyl-2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrithione (trithiobarbiturate, **1a**), besides the Paterno-Büchi product (1-thia-5,7-diazaspiro[3,5]nonane-6,8-dithione), a novel type of ring contraction product [thiohydantoin derivative; 1,3-dimethyl-5-(methylethylidene)imidazolidine-2,4-dithione (**2a**)] was obtained.[6] Since the thiohydantoin (**2a**) was also obtained in the absence of alkene, it was found that **1a** by oneself undergoes the ring contraction reaction to give **2a**. Similar ring contraction reaction has been also reported upon the photochemical reaction of oxygen analogs (5,5-disubstituted 2-methylbarbituric acid) in alkaline solution.[2c-e] The photochemical behavior of trithiobarbiturate, however, was considerably different from that of oxygen analog, that is, in the ring contraction mode, the loss of sulfur atom was involved in the former, whereas that of carbon monoxide in the latter. In this paper, we wish to report a facile photochemical transformation of various 5,5-disubstituted trithiobarbiturates (**1**) to thiohydantoin

derivatives (**2** and **3**), which were easily led to imidazolinothiophene derivatives (**4**).

5,5-Disubstituted trithiobarbiturates (**1a-f**) were obtained by the condensation of the corresponding disubstituted malonyl dichloride and 1,3-dimethylthiourea in the presence of triethylamine, followed by thionation of the monothiobarbiturate with the dimer of *p*-methoxyphenylthionophosphine (Lawesson's reagent).

Table 1. Physical Properties and Spectral Data for Trithiobarbiturates (**1a-f**)

	Substrate		mp	Appearance	MS (m/z)	Formula	Analysis (%)				^{1}H-NMR (90 MHz, $CDCl_3$) δ
			(℃)	(solvent)	M^+		Calcd (Found)				
	R^1	R^2					C	H	N	S	
1a	CH_3	H	45-46	Red prisms (hexane)	232	$C_8H_{12}N_2S_3$	41.38 (41.30	5.21 5.22	12.07 12.09	41.34 41.17)	1.76 (6H, s, CH_3x2), 4.20 (6H, s, NCH_3x2)
1b	Ph	H	119-121	Red prisms (hexane)	294	$C_{13}H_{14}N_2S_3$	53.06 (53.10	4.80 4.71	9.52 9.72	32.62 32.69)	2.06 (3H, s, CH_3), 4.14 (6H, s, NCH_3x2), 7.1-7.4 (5H, m, aromH)
1c	-$CH_2CH_2CH_2$-		47-48	Red prisms (hexane)	258	$C_{10}H_{14}N_2S_3$	46.51 (46.54	5.47 5.45	10.85 10.75	37.17 37.14)	1.7-1.9 (4H, m, C-CH_2-CH_2-C), 2.4-2.7 (4H, m, -$C\underline{H}_2CH_2CH_2C\underline{H}_2$-), 4.20 (6H, s, NCH_3x2)
1d	CH_3	CH_3	Oil		246	$C_9H_{14}N_2S_3$	246.0319[a] (246.0325)				0.82 (3H, t, *J*= 7.5 Hz, $CH_2C\underline{H}_3$), 1.87 (3H, s, CH_3), 2.12 (2H, q, *J*= 7.5 Hz, $C\underline{H}_2CH_3$), 4.19 (6H, s, NCH_3x2)
1e	CH_3	Ph	126-127	Red columns (hexane)	308	$C_{14}H_{16}N_2S_3$	54.54 (54.52	5.23 5.19	9.09 8.98	31.14 31.10)	2.16 (3H, s, CH_3), 3.25 (2H, s, $PhCH_2$), 3.97 (6H, s, NCH_3x2), 6.9-7.1 (2H, m, aromH), 7.1-7.4 (3H, m, aromH)
1f	C_2H_5	CH_3	Oil		260	$C_{10}H_{16}N_2S_3$	260.048[a] (260.045)				0.76 (6H, t, *J*= 7.5 Hz, $CH_2C\underline{H}_3$x2), 2.49 (4H, q, *J*= 7.5 Hz, $C\underline{H}_2CH_3$x2), 4,21 (6H, s, NCH_3x2)

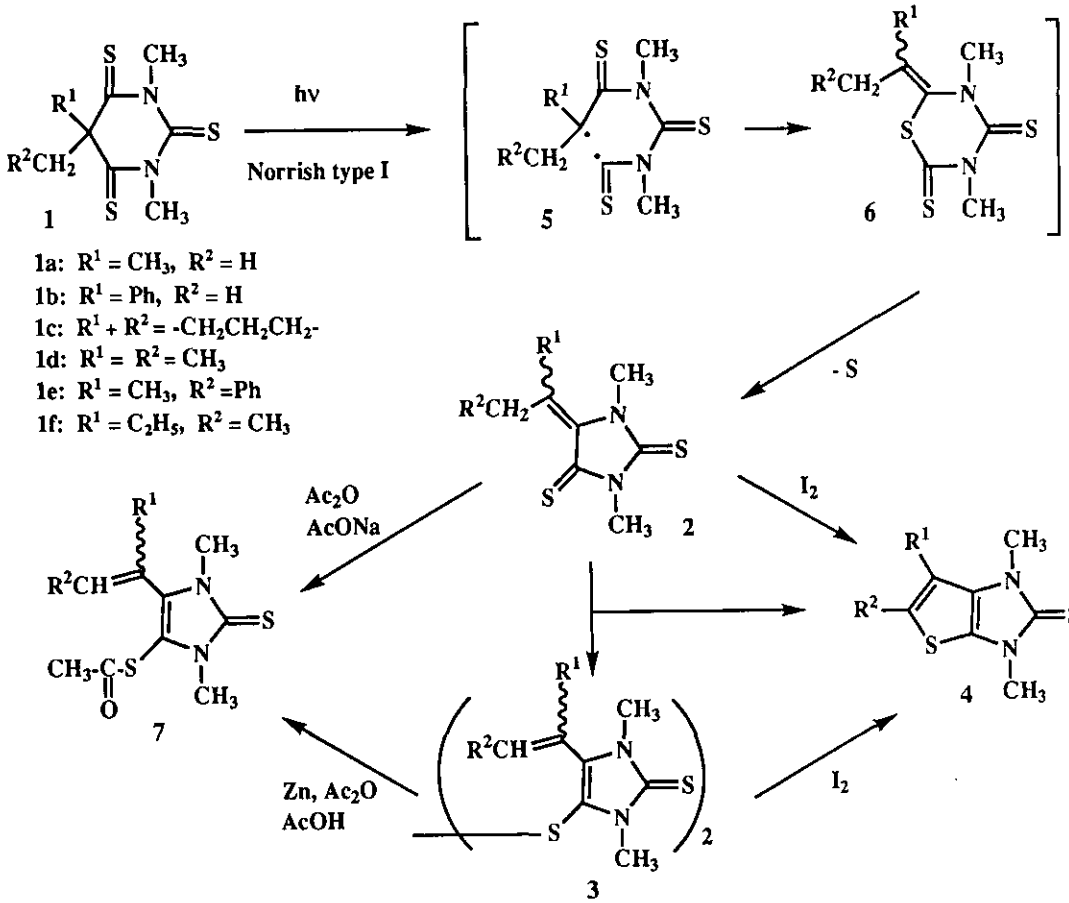
[a] Determined by high-resolution mass spectrometry. Upper figure, calcd for M^+; lower figure, found.

Photoreaction of **1** in acetone (10 mM) was carried out with 1 kW high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere for 0.25-3 h at room temperature. The results are listed in Table 2. Irradiation of 5,5-dimethyltrithiobarbiturate (**1a**) for 1.5 h gave thiohydantoin (**2a**) and a small amount of imidazolinothiophene derivative (1,3,6-trimethylthiopheno[3,2-*d*]imidazoline-2-thione, **4a**) in 68 and 2% yields, respectively, together with sulfur atom (67%). Similarly, trithiobarbiturate (**1b,c**) gave ring-contraction products (**2b,c**) in 48-70% yields accompanied by small amounts of **4b,c**, respectively. Further, in the cases of **1d-f**, the disulfides (**3d-f**), which presumably arose from thiohydantoin (**2d-f**),

were isolated in 29-88 % yields under the similar conditions. The formation pathway of **3** *via* **2** was suggested by the fact that acetylation of **2** afforded thioester (**7**), which was also derived from **3** by reduction of disulfide and subsequent acetylation (Scheme 1).

The structures of these products were determined on the basis of analytical and spectral data (Table 2, 3). The MS spectra of thiohydantoin (**2a-c**) showed molecular ion peaks (M^+) corresponding to the loss of sulfur atom from the trithiobarbiturate (**1a-c**). In the ^{13}C-NMR spectra of **2a-c**, the signals due to two olefinic carbons and two thiocarbonyl carbons appeared at 133.9-148.9 (s) and 177.3-185.1 (s), respectively. In the MS spectra, **3d-f** did not show a molecular ion peak, but displayed characteristic fragment peaks [(M^+/2)-1], which are consistent with the molecular weight of dehydrated products (**4d-f**), respectively. The ^{1}H-NMR spectra of **3d,3f** showed the signals due to one olefinic proton at 5.24-6.80 ppm, respectively, and the ^{13}C-NMR spectra of **3d-i** and **3e-i** exhibited signals due to one vinyl carbon,

Scheme 1



1a: $R^1 = CH_3$, $R^2 = H$
1b: $R^1 = Ph$, $R^2 = H$
1c: $R^1 + R^2 = -CH_2CH_2CH_2-$
1d: $R^1 = R^2 = CH_3$
1e: $R^1 = CH_3$, $R^2 = Ph$
1f: $R^1 = C_2H_5$, $R^2 = CH_3$

three olefinic carbons, and one 2-thiocarbonyl carbon at 133.4-137.2 (d), 113.8-143.2 (s), and 165.1-165.7 (s) ppm, respectively. Further, in the conversion of **3d** into **7d**, acetylation did not proceed without zinc dust. These results supported the conclusion that each structure of **3d-f** was a dimer of dithiohydantoins (**2d-f**).

Table 2. Photoreaction of Trichiobarbiturates **1** and Transformation of **2,3**, to the Thiophene Derivatives **4**

Photoreaction of **1**												Transformation **2** or **3** to **4**	
Substr-ate	Time (h)	Pro-duct	Yield (%)	mp (°C)	Appear-ance[a]	MS (m/z) M^+	Formula	Analysis (%) Calcd (Found) C	H	N	S	Time (h)	Yield (%)
1a	1.5	**2a**	68	125-127	Orange needles	200	$C_8H_{12}N_2S_2$	47.99 (47.90	6.05 6.07	14.00 14.00	31.97 31.70)	6.0	65
		4a	2	197-198	Colorless needles	198	$C_8H_{10}N_2S_2$	48.48 (48.39	5.09 5.09	14.14 14.31	32.29 32.22)		
1b	0.7	**2b**	48	116-117	Orange prisms	262	$C_{13}H_{14}N_2S_2$	59.53 (59.64	5.38 5.37	10.69 10.84	24.40 24.38)	12.0	77
		4b	4	132-134	Colorless needles	260	$C_{13}H_{12}N_2S_2$	59.99 (59.89	4.65 4.59	10.77 10.61	24.59 24.61)		
1c	3.0	**2c**	70	154-156 (dec.)	Orange needles	226	$C_{10}H_{14}N_2S_2$	53.08 (53.00	6.24 6.34	12.39 12.37	28.29 28.30)	12.0	78
		4c	1	186-187	Colorless needles	224	$C_{10}H_{12}N_2S_2$	53.56 (53.47	5.40 5.33	12.50 12.31	28.54 28.54)		
1d	0.8	**3d-i**[b]	41	134-136	Yellow columns	212[c]	$C_{18}H_{26}N_4S_4$	50.69 (50.64	6.15 6.26	13.15 13.09	30.01 30.05)	12.0	70
		4d	22	199-200	Colorless needles	212	$C_9H_{12}N_2S_2$	50.93 (50.83	5.70 5.67	13.21 13.23	30.16 30.31)		
1e	2.0	**3e-i**[d]	29	113-114	Orange needles	274[c]	$C_{28}H_{30}N_4S_4$	274.0598[e] (274.0575)				0.75	78
		4e	trace	209-211	Colorless needles	274	$C_{14}H_{14}N_2S_2$	61.30 (61.30	5.15 5.07	10.22 10.10	23.33 23.54)		
1f	0.25	**3f**[f]	88	133-135	Orange prisms	226[c]	$C_{20}H_{30}N_4S_4$	52.85 (52.72	6.66 6.78	12.33 12.12	28.16 28.21)	4.0	81
		4f	-	135-137	Colorless prisms	226	$C_{10}H_{14}N_2S_2$	53.08 (53.19	6,24 6.25	12.39 12.22	28 29 28.44)		

[a] Recrystallized from EtOH.

[b] **3d-i** was accompanied by a mixture (18%) of two rotational isomers of **3d-ii**.

[c] $[(M^+/2)-1]$.

[d] **3e-i** was accompanied by a mixture (13%) of two rotational isomers of **3e-ii**.

[e] Determined by high-resolution mass spectrometry. Upper figure, calcd for $[(M^+/2)-1]$; lower figure, found.

[f] A mixture of two geometrical isomers (**3f-i** and **3f-ii**) and their respective rotational isomers (**3f'-i** and **3f'-ii**) of **3f**.

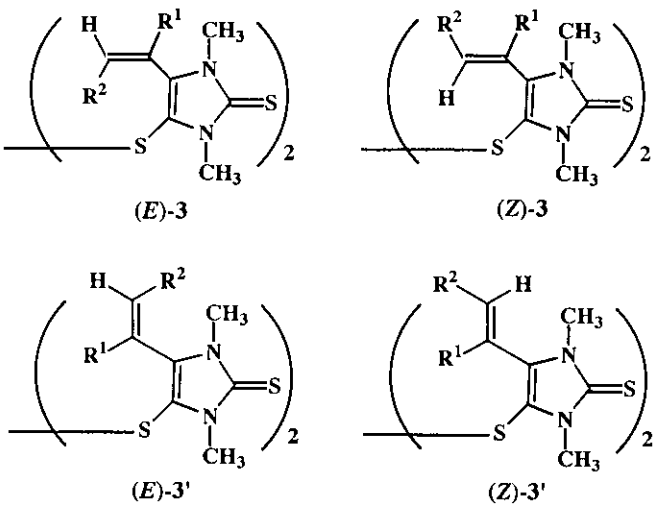
Table 3. NMR Spectral Data for the Compounds (**2a-c**, **3d-f**, and **4a-f**)

Compd.	^{1}H-NMR ($CDCl_3$, 90 MHz) δ	^{13}C-NMR ($CDCl_3$, 90 MHz) δ
2a	2.30 (3H, s, CH_3), 2.58 (3H, d, *J*= 0.9 Hz, CH_3), 3.67 (3H, s, NCH_3), 3.80 (3H, s, NCH_3)	25.6(q), 25.9(q), 33.5(q), 37.8(q),137.0(s), 137.3(s), 178.1(s), 184.3(s)
4a	2.42 (3H, d, *J*= 1.3 Hz, C=C-CH_3), 3.71 (3H, s, NCH_3), 3.87 (3H, s, NCH_3), 6.61 (1H, d, *J*= 1.3 Hz,C =CH-S)	14.2(q), 32.9(q), 34.0(q), 115.3(d), 121.7(s), 129.5(s), 132.1(s), 168.5(s)
2b	2.84 (3H, s, CH_3), 2.94 (3H, s, NCH_3), 3.74 (3H, s, NCH_3), 7.2-7.5 (5H, m, aromH)	25.7(q), 33.5(q), 37.8(q), 128.0(d)x2, 128.7(d)x2, 129.0(d), 136.2(s), 137.6(s), 142.0(s),178.4(s),185.1(s)
4b	3.58 (3H, s, NCH_3), 3.78 (3H, s, NCH_3), 6.85 (1H, s, C=CH-S), 7.43 (5H, s, aromH)	34.1(q)x2, 116.4(d), 128.3(s), 128.5(d), 128.7(d)x2, 129.2(d)x2, 130.2(s), 131.1(s), 133.7(s), 169.6(s)
2c	1.7-1.9 (4H, m, C-$CH_2\underline{CH_2}$-C), 2.7-3.0 (2H, m, C=C-CH_2), 2.9-3.2 (2H, m, C=C-CH_2), 3.70 (3H, s, NCH_3), 3.85 (3H, s, NCH_3)	26.3(t), 26.7(t), 33.5(q), 35.7(q), 35.7(t), 37.7(t), 133.9(s), 148.9(s), 177.3(s), 183.9(s)
4c	2.3-2.7 (2H, m, $CH_2\underline{CH_2}CH_2$), 2.7-3.1 (4H, m, CH_2-C=C-CH_2), 3.66 (3H, s, NCH_3), 3.72 (3H, s, NCH_3)	26.8(t), 28.3(t), 29.3(t), 33.2(q), 33.9(q), 128.1 (s), 128.3(s), 130.9(s), 136.7(s), 166.5(s)
3d-i	1.60 (3H, br s, CH_3), 1.75 (3H, dd, *J*= 7, 1 Hz, CH_3), 3.47 (3H, s, NCH_3), 3.65 (3H, s, NCH_3), 5.24 (1H, br q, *J*= 7 Hz, C=CH-C)	14.2(q), 16.4(q), 32.6(q), 33.4(q), 113.8(s), 122.1(s), 133.4(d), 143.2(s), 165.1(s)
3d-ii[a]	1.32 (3H, d, *J*= 6 Hz, CH_3), 1.38 (3H, dd, *J*= 6, 1 Hz, CH_3), 1.55 (3H, s, CH_3), 1.71 (3H, s, CH_3), 3.31 (3H, s, NCH_3), 3.33 (3H, s, NCH_3), 3.45 (3H, s, NCH_3),3.47 (3H, s, CH_3), 5.92 (1Hx2, br q, C=CH-C)	
4d	2.30 (3H, d, *J*= 0.9 Hz, CH_3), 2.39 (3H, s, CH_3), 3.68 (3H, s, NCH_3), 3.86(3H, s, NCH_3)	11.7(q), 13.7(q), 32.9(q), 34.0(q), 117.5(s), 125.4(s), 128.3(s), 132.4(s), 167.2(s)
3e-i	1.89 (3H, d, *J*=1 Hz, C=C-CH_3), 3.50 (3H, s, NCH_3), 3.62 (3H, s, NCH_3), 6.34 (1H, br q, *J*= 1 Hz, C=CH-C), 7.2-7.6 (5H, m, aromH)	18.2(q), 32.8(q), 33.7(q), 115.1(s), 122.6(s), 128.2(d), 128.6(d)x2, 129.3(d)x2, 135.3(s), 137.2(d), 143.1(s), 165.7(s)
3e-ii	1.81 (3H, d, *J*= 1.3 Hz, C=C-CH_3), 2.06 (3H, d, *J*= 1.3 Hz, C=C-CH_3), 3.37 (3H, s, NCH_3), 3.41 (3H, s, NCH_3), 3.48 (3H, s, NCH_3), 3.61 (3H, s, NCH_3), 6.7-7.0 (1Hx2, m, C=CH-C), 6.7-7.4 (5Hx2, m, aromH)	24.7(q), 25.1(q), 33.0(q), 33.2(q), 114.6(s), 115.8(s), 122.5(s), 122.9(s), 127.9(d)x2, 128.2(d), 128.8(d)x2, 135.6(s), 136.5(s), 137.0(d), 137.0(s), 138.4(s), 165.9(s), 166.1(s)
4e	2.45 (3H, s, CH_3), 3.70 (3H, s, NCH_3), 3.91 (3H, s, NCH_3), 7.40 (5H, s, aromH)	12.9(q), 33.1(q), 34.0(q), 117.6(s), 127.8(d), 128.0(s), 128.7(d)x2, 129.5(d)x2, 132.9(s), 133.2(s), 133.7(s), 168.1(s)
3f	0.6-1.1 (3Hx4, m, $CH_2\underline{CH_3}$), 1.34, 1.42, 1.72, 1.80 (3Hx4, br s, CH_3), 1.8-2.3 (2Hx4, m, $\underline{CH_2}CH_3$), 3.43, 3.44, 3.45, 3.47, 3.57, 3.60, 3.65, 3.68 (3Hx8, s, NCH_3), 4.9-5.3 (1Hx2, br q, C=CH-C), 5.7-6.1 (1Hx2, br q, C=CH-C)	
4f	1.19 (3H, t, *J*= 7 Hz, $CH_2\underline{CH_3}$), 2.40 (3H, s, CH_3), 2.71 (2H, q, *J*= 7 Hz, $\underline{CH_2}CH_3$), 3.69(3H, s, NCH_3), 3.86 (3H, s, NCH_3)	13.5(q), 15.4(q), 19.4(t), 33.0(q), 34.1(q), 124.5(s), 125.8(s), 128.1(s), 131.7(s), 167.2(s)

[a] ^{1}H-NMR (DMSO-d_6, 400 MHz)

As for a stereochemistry of disulfides (**3d-f**), the presence of two geometrical isomers [(*E*)-**3**, (*Z*)-**3**] and their respective rotational isomers [(*E*)-**3'**, (*Z*)-**3'**] is theoretically possible (Scheme 2). In the reactions of **2d,e**, only one rotational isomer (**3d-i**, **3e-i**) of **3d** and **3e** was isolated, respectively, however, it was difficult to assign **3d-i** and **3e-i** to one of the structures [(*E*)-**3**, (*Z*)-**3**, (*E*)-**3'**, and (*Z*)-**3'**] in Scheme 2. Furthermore, on standing in a chloroform solution at room temperature, the isolated **3d-i** and **3e-i** were easily converted to the corresponding other rotational isomers (**3d'-i** and **3e'-i**, respectively), reaching an equilibrium. Besides **3d-i** and **3e-i**, the other geometrical isomers (**3d-ii**, **3d'-ii** and **3e-ii**, **3e'-ii**) were obtained in the state of the rotational mixtures in 18 and 13% yields, respectively. In the ^{1}H-NMR spectra of these compounds (a mixture of **3d-ii** and **3d'-ii**, and a mixture of **3e-ii** and **3e'-ii**), two pairs of the methyl and NCH_3 signals were observed, respectively, suggesting the presence of two preferred conformers which are due to the restricted rotation about the C-C bond of a diene moiety. To confirm the existence of rotational isomer, the ^{1}H-NMR spectrum of **3d-ii** was measured at varied temperatures. At 90 ℃, two pair of dimethyl signals (1.32, 1.38 and 1.55, 1.71 ppm) and NCH_3 signals (3.31, 3.33 and 3.45, 3.47 ppm) of **3d-ii** coalesced into the one pair of signals of 1.36 (CH_3), 1.61(CH_3), 3.34 (NCH_3), and 3.46 (NCH_3) ppm, respectively. In the case of **2f**, the spectrum of product was observed as a mixture of two geometrical isomers and their respective inseparable rotational isomers (four pairs of NCH_3 signals existed), in which they could not be separated.

Scheme 2



It is well known that the systems having 1-mercapto-1,3-butadiene moiety are readily converted to thiophene derivatives in the presence of iodine catalyst.[7] In the present work, since imidazolinothiophene

derivatives (**4**) were photochemically obtained from **1** in poor yield, **2** or **3** was treated with iodine in dioxane at 100 ℃. As expected, **4** were obtained in good yields (Table 2).

The MS spectra of **4** showed the molecular ion peaks corresponding to the peaks dehydrated from **2** or **3**. The ^{1}H-NMR spectrum of **4a** revealed three methyl and one aromatic protons at 2.42, 3.71, 3.87 and 6.61 ppm, respectively, attributable to C-6 methyl protons, two NCH_3 protons, and C-5 proton of a thiophene ring. In the ^{13}C-NMR spectrum, **4a** indicated the peaks due to three methyl carbons [14.2 (q), 32.9 (q), and 34.0 (q)], and C-5 carbon in the thiophene ring [115.3 (d)], and three quaternary carbons [121.7(s), 129.5 (s), and 132.1 (s)] in addition to thiocarbonyl carbon [168.5 (s)]. Further, in the ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) spectrum (Figure 1), C-5 proton signal (δH 6.61 ppm) of thiophene ring showed cross peaks to C-6 methyl carbon (δC 14.2 ppm), C-3a (132.1 ppm), C-6 (121.7 ppm), and C-6a (129.5 ppm) quaternary carbons, respectively, and their correlations indicated the thiophene structure. The structures of **4b-f** were also assigned on the basis of spectral data, which were analogous to those of **4a**.

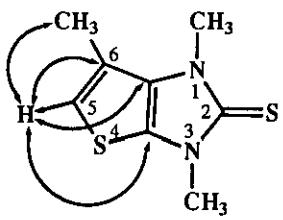


Figure 1. C-H Long-Range Correlations in the HMBC Spectrum of **4a**

A mechanism for this photochemical ring contraction reaction can be reasonably explained in terms of initial formation of 1,6-biradical intermediate (**5**) which was generated by α-cleavage (Norrish type I reaction) of a thiocarbonyl group (4-position of **1**), followed by recyclization to thiolactone (**6**), and then ring contraction leading to **2** or **3** with the loss of a sulfur atom (Scheme 1).

It is noteworthy that in the thiocarbonyl photochemistry, Norrish type I reaction appears to be very rare case, occurring in preference to the Paterno-Büchi reaction.[4,5,8] Although a few instances of Norrish type I reaction have been reported, they are limited to thiocarbonyl compounds, in which (S=)C-C bond is particularly weak as a result of high strain factors (three and four membered thioketones).[8] The present photoreaction involving unprecedented ring contraction also provides the first example of α-cleavage in a six-membered nitrogen-thiocarbonyl system such as trithiobarbiturate (**1**).

EXPERIMENTAL

All melting points were determined on a Yamato melting point apparatus (model MP-21) and are uncorrected. Infrared spectra were recorded on a JASCO A-102 spectrophotometer. Nuclear magnetic resonance spectra were taken on JEOL-FX-90Q, JEOL-LA-300, and JEOL JNM-EX 400 spectrometers. Chemical shifts are reported in ppm (δ) with tetramethylsilane as an internal standard. MS spectra were determined with a JEOL JMS-QH-100 gas chromatograph-mass spectrometer with a direct inlet system and high-resolution MS spectra were recorded using a JEOL JMS-DX 303 spectrometer. Irradiations of substrates were conducted using a 1 kW high-pressure mercury lamp and a water-cooled quartz immersion well (Eikosha EHB-W-1000). Stirring of the reaction mixture was effected by the introduction of a stream of nitrogen at the bottom of the outer jacket. All column chromatography was conducted using silica gel (Wakogel C-300, 200-300 mesh).

5,5-Disubstituted 1,3-dimethyl-2,4,6(1*H*, 3*H*, 5*H*)-pyrimidinetrithiones (Trithiobarbiturates 1a-f): General Procedure: i) Triethylamine (9.8 mL, 70 mmol) was added to a mixture of 2,2-disubstituted malonyl dichloride [prepared from the corresponding 2,2-disubstituted malonic acid (30 mmol) and phosphorus pentachloride] and 1,3-dimethyl-2-thiourea (3.4 g, 33 mmol) in benzene (30 mL) at 60 ℃. The reaction mixture was refluxed for 2 h, then treated with water and extracted with benzene. The organic layer was washed with saturated aqueous $NaHCO_3$, and brine, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel with AcOEt-hexane (1:10, v/v) to give 5,5-disubstituted 2,3-dihydro-1,3-dimethyl-2-thioxo-4,6(1*H*, 5*H*)-pyrimidinedione (monothiobarbiturate, **8**). The product was recrystallized from hexane; **8a** (R^1= CH_3, R^2= H): yield 54%, mp 78-79 ℃ (lit.,[3] mp 75-76.5 ℃); **8b** (R^1= Ph, R^2= H): yield 70%, mp 77-78 ℃; **8c** (R^1 + R^2= $-CH_2CH_2CH_2-$): yield 82%, mp 89-91 ℃; **8d** (R^1=CH_3, R^2= CH_3): yield 74%, mp 38-39 ℃; **8e** (R^1= CH_3, R^2= Ph): yield 73%, mp 155-157 ℃; **8f** (R^1= C_2H_5, R^2= CH_3): yield 43%, pale yellow oil.

ii) A solution of monothiobarbiturate (**8**) (15 mmol) and Lawesson's reagent (9.7 g, 24 mmol) in xylene (40 mL) was heated to reflux for 1-2 days. The solution was concentrated to one-third of its original volume, and the residue was directly subjected to column chromatography on silica gel to give **1**. Yields of **1a-f** and the solvent systems used were as follows: **1a**, 42%, AcOEt : hexane (1 : 20, v/v); **1b**, 7%, AcOEt : hexane (1 : 30, v/v); **1c**, 39%, AcOEt : hexane (1 : 30, v/v); **1d**, 54%, AcOEt : hexane (1 : 20, v/v); **1e**, 24%, AcOEt : hexane (1 : 20, v/v); **1f**, 6%, AcOEt : hexane (1 : 20, v/v). Melting points and analytical data of trithiobarbiturate (**1a-f**) are listed in Table 1.

Irradiation of Trithiobarbiturate Derivatives (1a-f): General Procedure Acetone solution of **1** (10 mM) was irradiated with a 1 kW high-pressure mercury lamp through a Pyrex filter with water cooling. After removal of the solvent *in vacuo*, the residue was subjected to silica gel column chromatography. The solvent systems used were as follows: **1a**, AcOEt : hexane = 1 : 8, v/v; **1b,c**,

AcOEt : hexane = 1 : 10, v/v; **1d**, AcOEt : hexane = 1 : 5, v/v; **1e,f**, AcOEt : hexane = 1 : 4, v/v.

Iodine Oxidation of Dithiohydantoins (2) and Its Disulfides (3) to Imidazolinothiophene Derivatives (4): General Procedure A solution of dithiohydantoin derivative (**2** or **3**) (0.27 mmol) and iodine (69 mg, 0.27 mmol) in dioxane (10 mL) was heated to reflux for 0.75-12 h. The solution was evaporated *in vacuo*, and the residue was chromatographed on silica gel with AcOEt : hexane (1 : 4, v/v) to give **4**. Melting points and analytical data of imidazolinothiophene (**4a-f**) are listed in Table 2.

Acetylation of Dithiohydantoin (2a); Formation of Thioester (7a) A mixture of dithiohydantoin (**2a**, 94 mg, 0.47 mmol), sodium acetate (82 mg, 1.00 mmol), and acetic anhydride (3 mL) was refluxed for 10 min. The reaction mixture was poured into ice-water, treated with K_2CO_3 to decompose excess of acetic anhydride, and extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel with AcOEt : hexane (1 : 4, v/v) to give thioester (**7a**) (102 mg, 84%). ^{1}H-NMR ($CDCl_3$, 90 MHz) δ: 1.96 (3H, d, *J*= 1.3 Hz, CH_3), 2.41 (3H, s, $COCH_3$), 3.53 (3H, s, NCH_3), 3.59 (3H, s, NCH_3), 5.10 (1H, s, =CH), 5.46 (1H, br s, =CH). ^{13}C-NMR ($CDCl_3$, 400 MHz) δ: 22.4(q), 29.5(q), 32.7(q), 33.5(q), 110.2(s), 122.7(t), 131.8(s), 139.1(s), 164.8(s), 192.6(s). MS *m/z*: 242 (M^+).

Acetylation of Dithiohydantoin Disulfide (3d-i) under Reductive Conditions A mixture of disufide (**3d-i**, 30 mg, 0.14 mmol), zinc dust (30 mg, 0.46 mmol), acetic acid (0.5 mL), and acetic anhydride (0.5 mL) was refluxed for 15 min. The reaction mixture was poured into ice-water, treated with K_2CO_3 to decompose excess of acetic anhydride, and extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel with AcOEt : hexane (1 : 4, v/v) to give thioester (**7d**) (28 mg, 78%). ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.78 (3H, dd, *J*= 7, 1 Hz, CH_3), 1.82 (3H, s, CH_3), 2.40 (3H, s, $COCH_3$), 3.52 (3H, s, NCH_3), 3.54 (3H, s, NCH_3), 5.62 (1H, qd, *J*= 7, 1 Hz, =CH). ^{13}C-NMR ($CDCl_3$, 400 MHz) δ: 14.0(q), 16.3(q), 29.4(q), 32.7(q), 33.4(q), 109.8(s), 123.0(s), 132.5(d), 141.1(s), 164.4(s), 193.1(s). MS *m/z*: 256 (M^+).

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