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INTRAMOLECULAR PHOTOREACTION OF THIOBARBITURATES WITH AN ALKENYL OR A BENZYL GROUP IN THEIR *N*-Alkyl SIDE CHAIN. REGIOSELECTIVE SYNTHESIS OF RING-FUSED PYRIMIDINE DERIVATIVES THROUGH PHOTOCYCLIZATION OF MONO- AND DI-THIOBARBITURATES[1]

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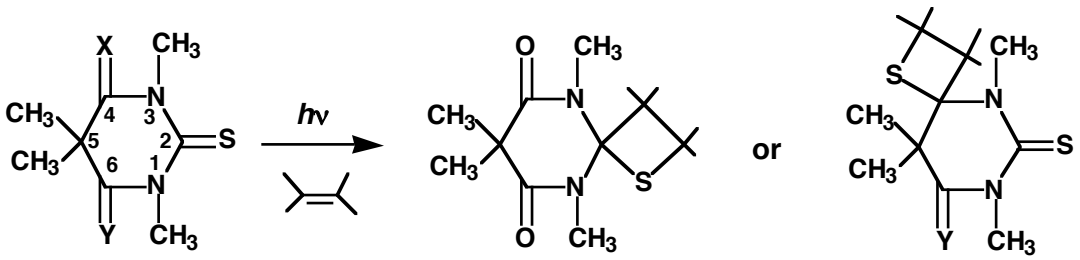
Abstract- Upon irradiation, thiobarbiturates with an alkenyl (**4,5**) or a benzyl (**14,15,21**) group in their *N*-alkyl side chain give bi- and tri-cyclic fused pyrimidine derivatives through regioselective [2+2] photocycloaddition or Norrish type II reaction, respectively.

During the course of our systematic studies on the photochemistry of nitrogen-thiocarbonyl systems, we found that the major photochemical processes of the cyclic thioimides[2] and aromatic thioamides[3] are limited to [2+2] photocycloaddition (Paterno-Büchi reaction) with olefins, although certain thioimides having a benzylic hydrogen in the *N*-alkyl side chain undergo the Norrish type II reaction to give cyclized products.[2e,4] As an extension of this work, our finding led us to investigate the photoreaction of thiobarbiturates,[5] whose skeletons consist of a combination of a thioimide and an amide or a thioamide. In this system it was found that the intermolecular thietane formation occurred regioselectively, i.e., in the case of 2-monothiobarbiturate (**1a**), photoaddition of olefin occurred only at the 2-position to give thietane (**2a**), whereas for 2,4-di- and 2,4,6-trithiobarbiturates (**1b** and **1c**), the resulting thietanes (**3b** and **3c**) were the products reacting with the 4-thiocarbonyl (Scheme 1). As an application of this regioselective reaction, the construction of various diaza-heterocycles was examined through the intramolecular photocyclization of thiobarbiturates with an alkenyl group in their *N*-alkyl side chain.[6] The present report is concerned with the detailed results of intramolecular Paterno-Büchi and intramolecular Norrish type II cyclization reactions in these thiobarbiturate systems.

A series of thiobarbiturate derivatives (**4,5,14**, and **15**) were prepared from 2,3-dihydro-1,5,5-trimethyl-

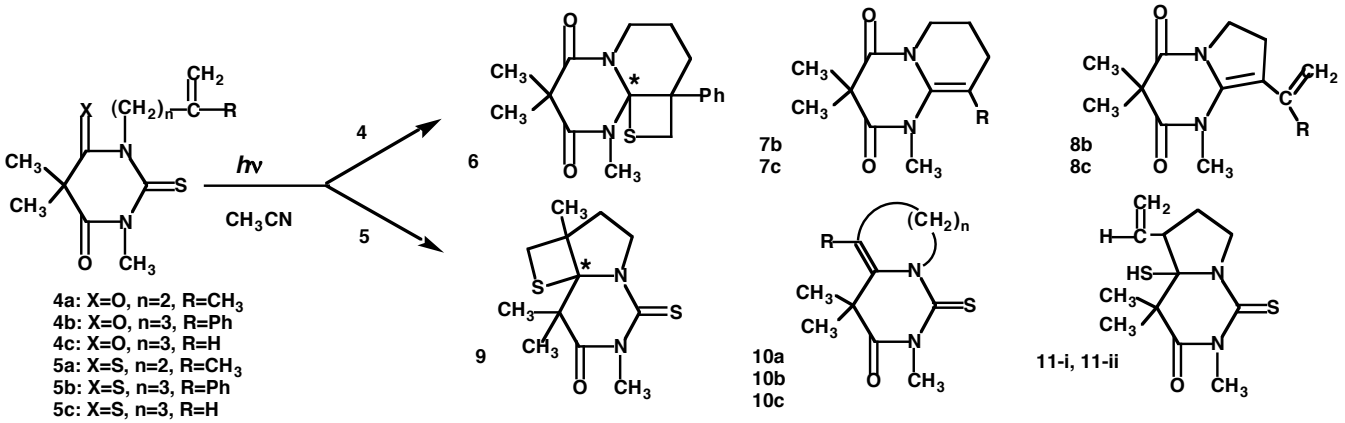
Scheme 1



2-thioxo-4,6(1*H*, 5*H*)-pyrimidinedione or 2,3,4,5-tetrahydro-1,5,5-trimethyl-2,6-dithioxo-4(1*H*)-pyrimidinone and the appropriate alcohols, respectively. Substrates (**21a** and **21b**) were obtained by the thionation of 2,3-dihydro-1,3,5-trimethyl-5-(ω-phenylalkyl)-2-thioxo-4,6(1*H*,5*H*)-pyrimidinedione which were prepared from the corresponding methyl(ω-phenylalkyl)methane-1,1-dicarbonyl chloride and 1,3-dimethyl-2-thiourea. The yields and analytical data of thiobarbiturates (**4**,**5**,**14**,**15**, and **21**) are listed in Table 1.

Photolyses of thiobarbiturates (**4**,**5**,**14**,**15**, and **21**) were performed in acetonitrile (10 mM) using a 1 kW high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere at room temperature. The results are shown in Scheme 2, Scheme 4, and Table 2.

Scheme 2



In the photoreaction of *N*-(4-phenyl-4-pentenyl)monothiobarbiturate (**4b**), the [2+2] cycloaddition of olefin moiety occurred at the 2-thiocarbonyl (C=S) in preference to the 4-carbonyl (C=O), giving the corresponding tricyclic thietane (**6**) in 34% yield, accompanied by dethioformylated enamide compound (**7b**) in 26% yield. Probably the compound (**7b**) arises from the initially formed **6** through photochemical fission (cycloreversion) of the thietane ring.[5] Interestingly, besides the Paterno-Büchi products (**6** and **7b**),

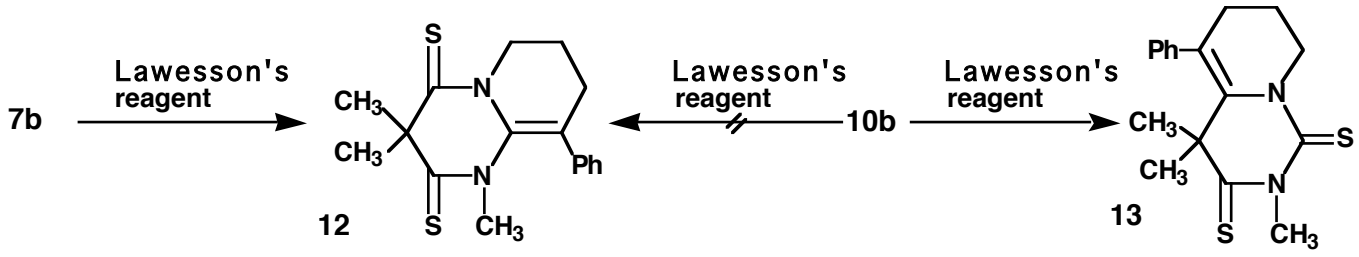
trace amounts of diene compound (**8b**), which arose by elimination of hydrogen sulfide from the initially formed intramolecular Norrish type II product (thiol), were also obtained. Similarly, in the case of *N*-(4-pentenyl)monothiobarbiturate (**4c**), dethioformylated compound (**7c**) was obtained in 36% yield together with the Norrish type II product (**8c**, 3%). However, *N*-(3-methyl-3-butenyl)monothiobarbiturate (**4a**), having a shorter *N*-alkyl side chain than ones of **4b** and **4c**, yielded a complex photolysate, and isolable products were not obtained.

Next, photolyses of dithiobarbiturates (**5**) having both 2-thiocarbonyl and 4-thiocarbonyl groups were examined. Photoaddition of alkenyl group in dithiobarbiturate (**5a**) occurred only at the 4-position to give tricyclic thietane (**9**) and dethioformylated bicyclic ene-thioamide compound (**10a**) in 18 and 46% yields, respectively. Similarly, photolyses of **5b** and **5c** afforded the dethioformylated cyclic ene-thioamides (**10b,c**) in 37 and 21% yields, respectively. In addition, in **5c**, Norrish type II product, thiol compound (**11-i**) was also obtained in 20% yield, together with a trace of its isomer (**11-ii**).

The structures of all products were determined on the basis of the spectral and analytical data (Table 2 and Table 3). The MS spectra of thiethanes (**6** and **9**) and thiol compound (**11-i**) showed the molecular ion peaks at *m/z* 330 (**6**), 270 (**9**), and 270 (**11-i**) corresponding to the molecular weights of **4b**, **5a**, and **5c**, respectively. Cyclic enamide and ene-thioamide compounds (**7b**,**c**, and **10a-c**) and conjugated diene compounds (**8b**,**c**) showed the peaks corresponding to the molecular formula which was equivalent to the loss of thioformaldehyde or hydrogen sulfide from the initially formed thiethanes or thiols, respectively. The formations of the thiethane ring in **6** and **9** were confirmed by the NMR spectra (Table 3). In the ^{1}H-NMR spectra of thiethanes (**6** and **9**), the signals due to methylene protons of newly formed thietane ring appeared at δ 2.96 and 3.71 (each 1H, d, *J*= 9.7 Hz), and 2.71 and 3.06 (each 1H, d, *J*= 9.0 Hz), instead of signals due to olefinic protons in the *N*-alkyl side chains of **4b** and **5a**, respectively. Further, as regarding **6**, it was observed that a signal due to one of the methylene protons has shifted to downfield (δ 3.71) as compared with that of **9** (δ 3.06), owing to the anisotropic effect of the benzene ring. The position of a thiocarbonyl group reacting with a carbon-carbon double bond moiety was confirmed by comparison of ^{13}C-NMR spectra. For **6**, a signal due to a quaternary carbon atom (*) adjacent to two nitrogens and a sulfur atom appeared at δ 88.4 (s), whereas the corresponding signal of **9** appeared at upfield [δ 80.7 (s)] in comparison with that of **6**. This difference in the chemical shift between **6** and **9** was also observed in those of thietane rings in the previously reported 1-thia-5,9-diazaspiro[3,5]nonane (**2**) and 1-thia-5,7-diazaspiro[3.5]nonane (**3**) systems.[4] For the cyclic enamide and ene-thioamide compounds (**7b**,**c**, and **10a-c**), each ^{13}C-NMR spectrum showed the singlet peaks due to the sp^2 carbon adjacent to one or two nitrogens at δ 131.1-138.6. The ^{1}H-NMR spectrum of **10b** showed a singlet due to 5-methyl protons at an upfield (δ 1.08), owing to an anisotropic effect of the benzene ring, however, this upfield shift was not observed in **7b** (δ 1.50). To confirm the reaction site, the products (**7b** and **10b**) were treated with Lawesson's reagent, respectively (Scheme 3). The thionation product (**12**) derived from **7b** was not identical with the dithio compound (**13**) from **10b**. This indicated that the photocycloaddition occurred at

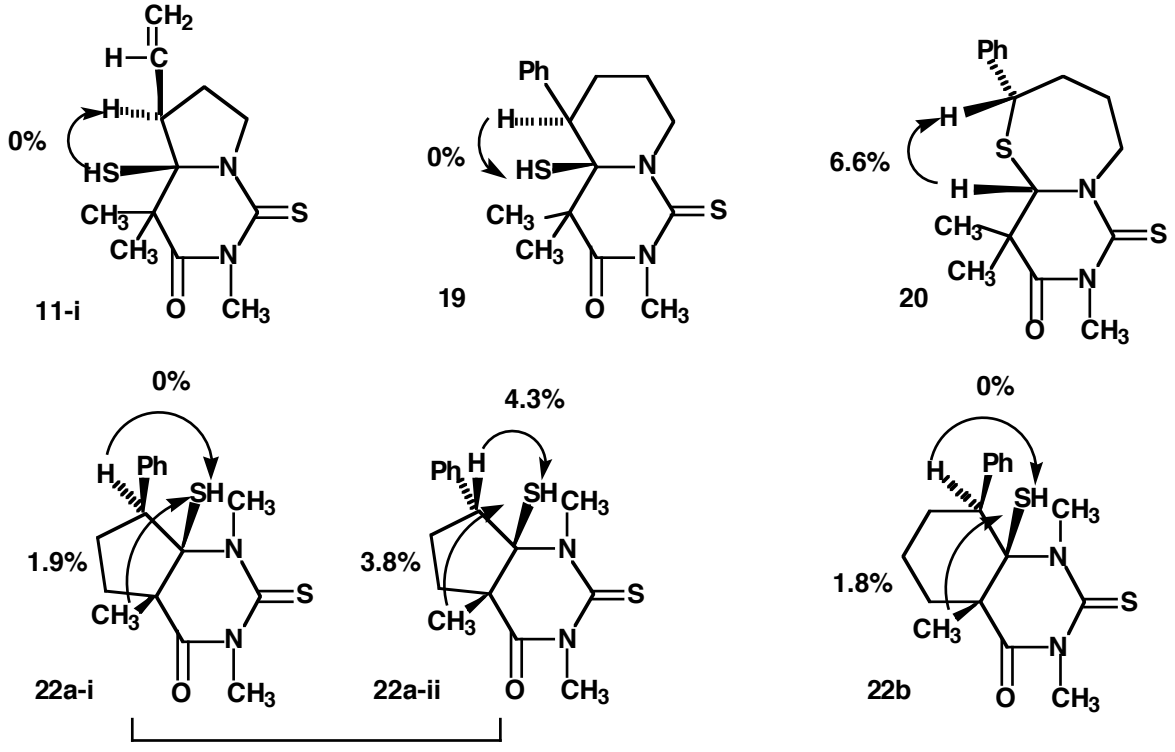
the 2-position in monothiobarbiturate (**4**), and at 4-position in dithiobarbiturate (**5**), respectively.

Scheme 3



In regard to the diene compounds (**8b** and **8c**), the ^{1}H-NMR spectra showed characteristic signal due to terminal vinyl protons at δ 5.25 and 5.72 (each 1H, d, *J*= 1.3 Hz) and 4.9-5.1 (2H, m), respectively. Further, in the ^{13}C-NMR spectra, the singlet peaks due to the sp^2 carbons adjacent to two nitrogens and the other sp^2 carbons on pyrroline ring appeared at δ 131.2-132.0 and 103.1-103.7, respectively. The ^{1}H-NMR spectrum of thiol compound (**11-i**) showed peaks due to thiol and vinyl protons at δ 1.96 (1H, s, SH), 5.2-5.4 (2H, m, CH_2=C-) and 5.9-6.1 (1H, m, CH_2=C<u>H</u>-), respectively. Further, nuclear Overhauser effect (NOE) was not observed between the methine proton (δ 3.2-3.3) and thiol proton (δ 1.96), indicating that the configuration of a vinyl and a thiol group in **11-i** is cis as shown in Figure 1.

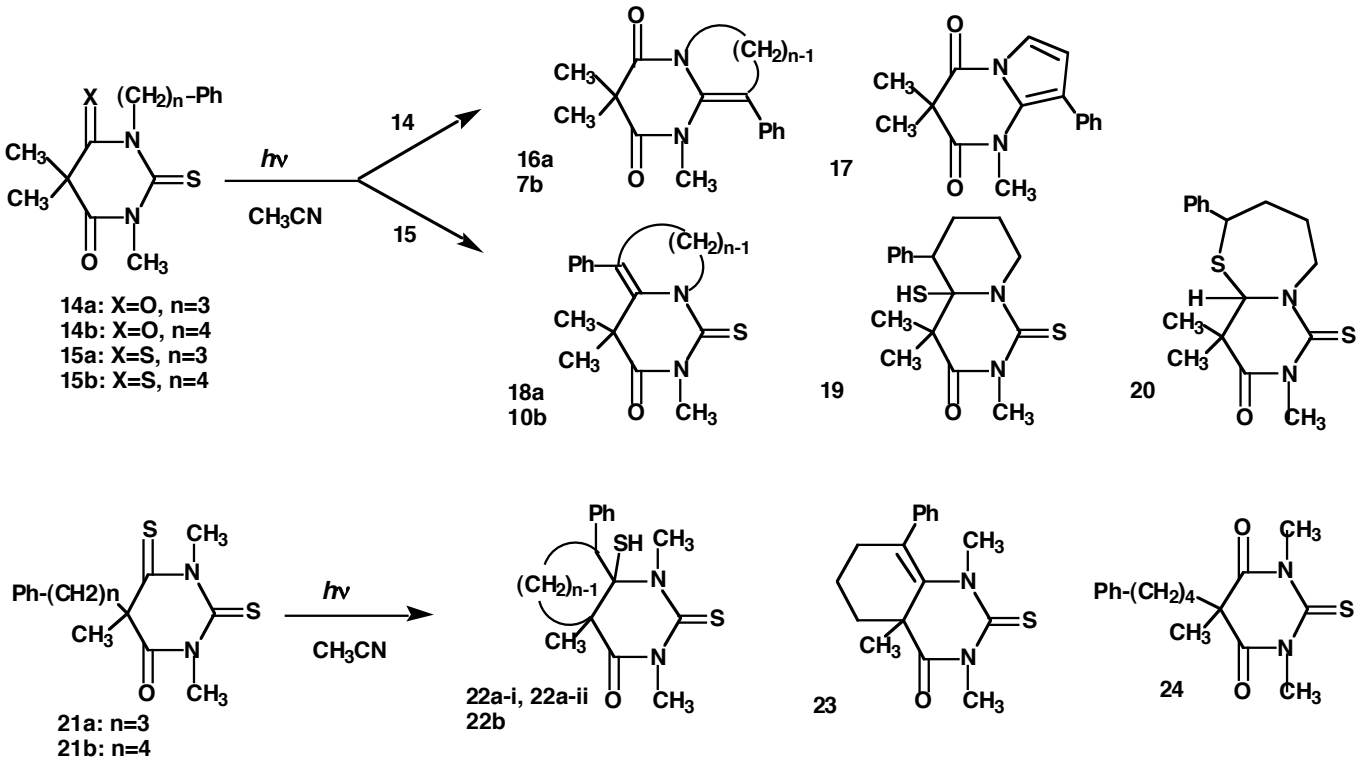
Figure 1. NOEs observed in cyclized Products



As observed in the present work, certain thiobarbiturates (**4b**,**c** and **5c**) possessing three methylene

carbons in their *N*-ω-alkenyl side chain underwent not only [2+2] cycloaddition but also Norrish type II reaction to give cyclized compounds. Therefore, to investigate the scope of this Norrish type II reaction, the photoreaction of thiobarbiturates (**14** and **15**) having a benzylic hydrogen in their *N*-alkyl side chain was examined (Scheme 4). As expected, photolyses of monothiobarbiturates (**14a**,**b**) gave bicyclic pyrimidine

Scheme 4

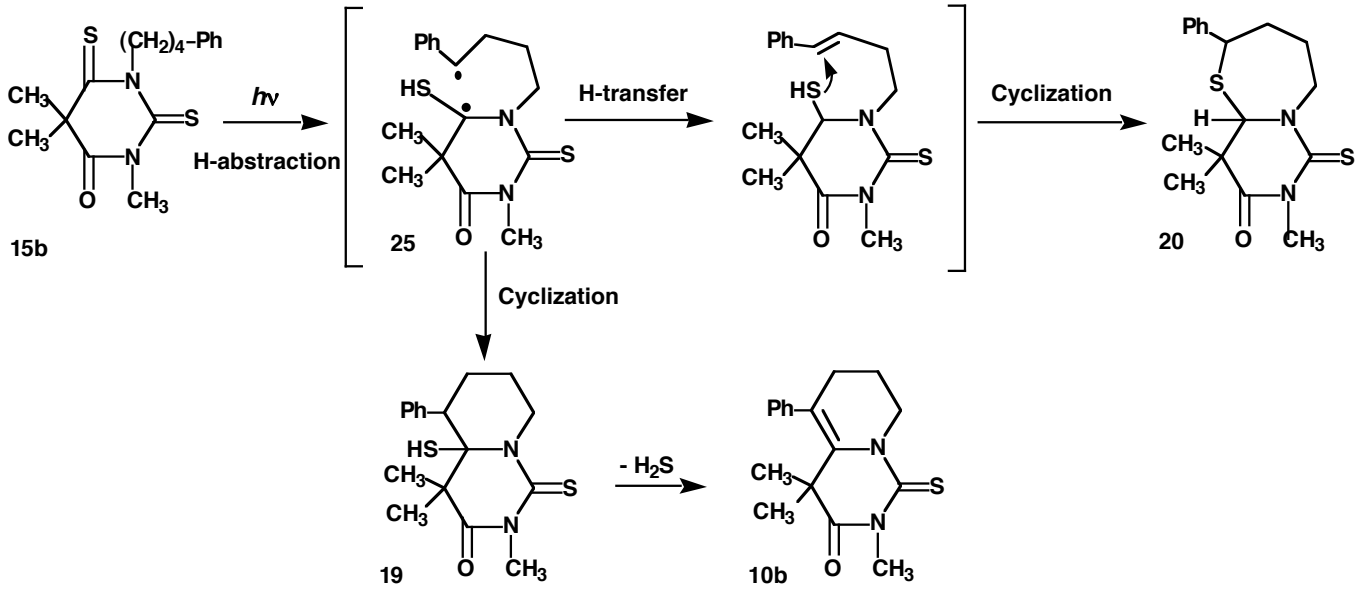


derivatives (**16a,7b**) in 78 and 40% yields, respectively. The reaction resulted in the C-C bond formation between the 2-thiocarbonyl and the benzylic carbon in their *N*-alkyl side chain, followed by elimination of hydrogen sulfide from initially formed thiol compound corresponding to Norrish type II product. In the case of **14a**, pyrrole derivative (**17**) was also obtained in 6% yield, apparently derived from the initially formed **16a** through photochemical and/or thermal oxidative dehydrogenation. On the other hand, **15a** (dithio analog of **14a**) underwent benzylic hydrogen abstraction at the 4-thiocarbonyl group, giving a cyclic ene-thioamide (**18a**) in 23% yield. Further, in the reaction of **15b**, both thiol (**19**) and ene-thioamide (**10b**) were obtained in 8 and 13% yields, respectively, accompanied by unexpected cyclic thioether (**20**) in 9% yield. The mechanism for formation of **20** can be reasonably explained in terms of initial formed 1,6-biradical intermediate (**25**) which was generated by benzylic hydrogen abstraction of a 4-thiocarbonyl group, followed by hydrogen transfer, and then addition of thiol group to the intramolecular olefinic carbon leading to **20** (Scheme 5).

Further, to investigate the synthesis of a variety of ring-fused pyrimidine derivatives, photolyses of dithiobarbiturates (**21a**,**b**) having a benzylic hydrogen in their C-5-alkyl side chain were performed. In

these systems, each abstraction from benzylic hydrogen occurred only at the 4-thiocarbonyl group, giving

Scheme 5



the corresponding thiols [**22a-i**: 25%, **22a-ii**: 23%, and **22b**: 12%] and cyclic ene-thioamide (**23:** 6%). Further, **21b** also gave the oxidative desulfurization product (**24**) in 9% yield (Scheme 4).

The structures of these products were determined on the basis of the spectral and analytical data (Table 2 and Table 3). Spectral data of **7b** (from **14b**) and **10b** (from **15b**) were in agreement with those of the products obtained from **4b** and **5b**, respectively.

The MS spectra of **16-20** and **22-24** showed the peaks corresponding to the molecular formula of each compound. The structures of the thiols (**19**, **22a-i**, **22a-ii**, and **22b**) were confirmed by the NMR spectra (Table 3). Their ^{1}H-NMR spectra showed peaks due to thiol and benzylic protons at δ 2.17-2.54 (SH) and 3.2-3.6 (PhCH-), respectively. In addition, the ^{13}C-NMR spectra showed peaks due to a benzylic carbon and a quaternary carbon adjacent to a nitrogen and a sulfur atom at δ 47.3-58.8 (d) and 77.5-83.9 (s), respectively. The stereochemistries of thiol compounds were assigned from the NOE experiments (Figure 1). In the spectrum of **22a-i** , irradiation at the signal of the methine proton [δ 3.56 (1H, t)] enhanced hardly the signal intensity of the thiol proton [δ 2.17 (1H, s)]. In **22a-ii**, on irradiation at the methine proton [δ 3.5-3.6 (1H, m)] a 4.3% increment of the thiol signal [δ 2.54 (1H, s)] was observed. Further, the NOE enhancement was observed between the signals of the methyl proton and thiol proton in each isomer (**i** and **ii**). This NMR spectroscopy supported the structures of **22a-i** and **22a-ii** as shown in Figure 1. Similarly, the stereochemistries of other thiols (**19** and **22b**) were determined by the NOE experiments (Figure 1).

The ^{13}C-NMR spectra of cyclic enamide and ene-thioamides (**16a**,**18a**, and **23**) were analogous to those of **7b**,**c** and **10a-c**, that is, the singlet peaks due to the sp^2 carbon adjacent to one or two nitrogens and its

adjacent sp^2 carbons appeared at δ 130.6-135.8 and 104.0-130.5 respectively. Further, the spectrum of pyrrole derivative (**17**) showed two doublet signals at δ 111.8 and 116.6, besides two singlet signals of sp^2 carbons (each δ =130.1 and 112.2) as mentioned above, indicated the presence of pyrrole moiety. The structural assignment of cyclic thioether (**20**) was based on the following data. The HRMS gave analytical value corresponding to the molecular formula of **20**. The ^{1}H-NMR spectrum of **20** showed peaks due to a benzylic proton, and a methine proton adjacent to a nitrogen and a sulfur atom at δ 4.11 (1H, dd, *J*= 10.3, 1.5 Hz) and 4.76 (1H, s), respectively. In addition, the ^{13}C-NMR spectrum showed two doublet peaks due to two methine carbons adjacent to a sulfur atom at δ 51.4 (d) and 71.4 (d), and two singlet peaks due to carbony and thiocarbonyl carbons at δ 170.8 (s) and 179.8 (s), respectively. IR spectrum showed the presence of monothioimide (-N-C=O) at 1694 cm^{-1}, and the absence of thiol group. Further, a 6.6% NOE enhancement was observed between the two methine protons (δ 4.11 and 4.76), supporting the stereostructure of **20** as shown in Figure 1.

In conclusion, this regioselective photocyclization could provide a useful method for the construction of a variety of ring-fused pyrimidine derivatives, i.e., pyridino[1,2-*a*]pyrimidine, pyrrolino[1,2-*a*]pyrimidine, pyridino[1,2-*c*]pyrimidine, pyrrolino[1,2-*c*]pyrimidine, pyridino[1,2-*d*]pyrimidine, pyrrolino[1,2-*d*]-pyrimidine, otherwise inaccessible by conventional thermal reaction.

Table 1. Physical Properties and Spectral Data for Thiobarbiturates (**4**,**5**,**14**,**15**, and **21**)

Substrate	Yield (%)	mp (° C)	MS (*m/z*) M^+	Formula	HRMS Calcd (Found)	^{1}H-NMR (90 MHz, $CDCl_3$) δ
4a	77	Yellow oil	254	$C_{12}H_{18}N_2O_2S$	254.1089 (254.1094)	1.55 (6H, s, CH_3x2), 1.81 (3H, s, C=CCH_3),2.3-2.4 (2H, m, C=C-CH_2-), 3.67 (3H, s, NCH_3), 4.4-4.5 (2H, m, NCH_2-), 4.72 (1H, s, C=CH_2), 4.79 (1H, s, C=CH_2)
4b	74	Yellow oil	330	$C_{18}H_{22}N_2O_2$ S	330.1402 (330.1379)	1.52 (6H, s, CH_3x2), 1.6-2.0 (2H, m, $NCH_2C\underline{H}_2$-), 2.56 (2H, t, *J*= 7.5 Hz, C=C- CH_2-), 3.64 (3H, s, NCH_3), 4.3-4.5 (2H, m, NCH_2-), 5.1 and 5.3 (2H,) br s, C=CH_2), 7.2-7.5 (5H, m, ArH)
4c	81	Yellow oil	254	$C_{12}H_{18}N_2O_2S$	25 4.1089 (254.1086)	1.55 (6H, s, CH_3x2), 1.7-1.8 (2H, m, $NCH_2C\underline{H}_2$-), 2.1-2.2 (2H, m, C=C-CH_2-), 3.67 (3H, s, NCH_3), 4.3-4.4 (2H, m, NCH_2-), 4.9-5.1 (2H, m, C=CH_2), 5.8-5.9 (1H, m, CH_2=C$\underline{H}$-)
5a	33	Orange oil	270	$C_{12}H_{18}N_2OS_2$	270.0860 (270.0846)	1.64 (6H, s, CH_3x2), 1.81 (3H, s, CH_3), 2.3-2.6 (2H, m, C=C-CH_2-), 3.66 (3H, s, NCH_3), 4.7-4.9 (2H, m, C=CH_2), 4.9-5.1(2H, m, NCH_2-)
5b	51	Orange oil	346	$C_{18}H_{22}N_2OS_2$	346.1174 (346.1248)	1.60 (6H, s, CH_3x2), 1.7-2.1 (2H, m, $NCH_2C\underline{H}_2$-), 2.58 (2H, t, *J*= 7.5 Hz, C=C-CH_2-), 3.62 (3H, s, NCH_3), 4.8-5.1 (2H, m, NCH_2-), 5.11 (1H, d, *J*= 1.3 Hz, C=CH_2), 5.30 (1H, br s, C=CH_2),

Table 1. Continued

Substrate	Yield (%)	mp (° C)	MS (*m/z*) M^+	Formula	HRMS Calcd (Found)	^{1}H-NMR (90 MHz, $CDCl_3$) δ
						7.2-7.5(5H, m, ArH)
5c	55	Orange oil	270	$C_{12}H_{18}N_2OS_2$	270.0861 (270.0860)	1.64 (6H, s, CH_3x2), 1.8-1.9 (2H, m, $NCH_2C\underline{H}_2$-), 2.1-2.2 (2H, m, C=C-CH_2-), 3.65 (3H, s, NCH_3), 4.9-5.0 (2H, m, NCH_2-), 4.9-5.1 (2H, m, C=CH_2), 5.8-5.9 (1H, m, CH_2=C$\underline{H}$-)
14a	80	Pale yellow prisms 125-127	304	$C_{16}H_{20}N_2O_2S$	304.1246 (304.1245)	1.52 (6H, s, CH_3x2), 1.9-2.1 (2H, m, $NCH_2C\underline{H}_2$-), 2.68 (2H, t, *J*= 7.8 Hz, $PhCH_2$-), 3.64 (3H, s, NCH_3), 4.3-4.5 (2H, m, NCH_2-), 7.1-7.4 (5H, m, ArH)
14b	82	Pale yellow prisms 73-74	318	$C_{17}H_{22}N_2O_2S$	318.1402 (318.1340)	1.5-1.9 (4H, m, $NCH_2C\underline{H}_2C\underline{H}_2$-), 1.53 (6H, s, CH_3x2), 2.5-2.8 (2H, m, $PhCH_2$-), 3.65 (3H, s, NCH_3), 4.2-4.5 (2H, m, NCH_2-), 7.0-7.4 (5H, m, ArH)
15a	48			$C_{16}H_{20}N_2OS_2$	320.1017 (320.0989)	1.62 (6H, s, CH_3x2), 2.0-2.2 (2H, m, $NCH_2C\underline{H}_2$-), 2.68 (2H, t, *J*= 7.8 Hz, $PhCH_2$-), 3.63 (3H, s, NCH_3), 4.9-5.0 (2H, m, NCH_2-), 7.1-7.4 (5H, m, ArH)
15b	49	Orange prisms 56-57	334	$C_{17}H_{22}N_{2O}S_2$	334.1174 (334.1164)	1.5-1.9 (4H, m, $NCH_2C\underline{H}_2C\underline{H}_2$-), 1.63 (6H, s, CH_3x2), 2.6-2.7 (2H, m, $PhCH_2$-), 3.65 (3H, s, NCH_3), 4.9-5.0 (2H, m, NCH_2-), 7.1-7.4 (5H, m, ArH)
21a	43	Orange prisms 66-67.5	320	$C_{16}H_{20}N_{2O}S_2$	320.1017 (320.1001)	1.2-1.8 (2H, m, $PhCH_2C\underline{H}_2$-), 1.68 (3H, s, CH_3), 2.0-2.3 (2H, m, $PhCH_2CH_2C\underline{H}_2$-), 2.55 (2H, t, *J*= 7.5 Hz, $PhCH_2$-), 3.64 (3H, s, NCH_3), 4.19 (3H, s, NCH_3), 7.0-7.4 (5H, m, ArH)
21b	48	Orange oil	334	$C_{17}H_{22}N_{2O}S_2$	334.1173 (334.1196)	0.9-1.7 (4H, m, $PhCH_2C\underline{H}_2C\underline{H}_2$-), 1.70 (3H, s, CH_3), 2.0-2.2 (2H, m, CH_3C-C$\underline{H}_2$-), 2.55 (2H, t, *J*= 7.5 Hz, $PhCH_2$-), 3.64 (3H, s, NCH_3), 4.19 (3H, s, NCH_3), 7.0-7.4 (5H, m, ArH)

Table 2. Physical Properties and Spectral Data for Products (**6-11**, **16-20**, and **22-24**)

Substrate	Time (h)	Product	Yield (%)	mp (°C)	IR (Nujol) (cm^{-1})	M(*m/z*) M^+	Formula	Analysis Calcd (Found) C	H	N	S
4b	1.17	**6**	34	125-127	1670 1640	330	$C_{18}H_{22}N_2O_2S$	65.43 (65.42	6.72 6.74	8.48 8.34	9.68 9.83)
		7b	26	112-114	1695 1655	284	$C_{17}H_{20}N_2O_2$	71.80 (71.85	7.09 7.10	9.85 9.98)	
		8b	trace	oil		296					
4c	0.67	**7c**	36	oil	1698 1650	208	$C_{11}H_{16}N_2O_2$	208.1212[a)] (208.1208)			

Table 2. Continued

Substrate	Time (h)	Product	Yield (%)	mp (°C)	IR (Nujol) (cm^{-1})	M(*m/z*) M^+	Formula	Analysis Calcd (Found) C	H	N	S
		8c	3	87-90	1686, 1646 1626	220	$C_{12}H_{16}N_2O_2$	220.1212[a)] (220.1208)			
5a	0.25	**9**	18	174-176	1695	270	$C_{12}H_{18}N_2OS_2$	53.32 (53.22	6.72 6.65	10.37 10.17	23.68 23.61)
		10a	46	68-69.5	1695,1680 1655	224	$C_{11}H_{16}N_2OS$	58.90 (58.96	7.20 7.26	12.50 12.35	14.27 14.06)
5b	0.67	**10b**	37	126-127	1700	300	$C_{17}H_{20}N_2OS$	67.97 (67.86	6.72 6.85	9.33 9.29	10.65 10.65)
5c	0.25	**10c**	21	89-90.5	1701 1660	224	$C_{11}H_{16}N_2OS$	58.90 (58.86	7.19 7.19	12.49 12.45	14.29 14.65)
		11-i	20	semisolid	1705	270	$C_{12}H_{18}N_2OS_2$	270.0861[a)] (270.0858)			
		11-ii	trace								
14a	0.28	**16a**	78	124-126	1696 1655, 1640	270	$C_{16}H_{18}N_2O_2$	71.09 (71.16	6.71 6.93	10.36 10.28)	
		17	6	102-104	1735 1670	268	$C_{16}H_{16}N_2O_2$	268.1212[a)] (268.1216)			
14b	0.7	**7b**	40								
15a	1.5	**18a**	23	121-123	1690 1660	286	$C_{16}H_{18}N_2OS$	67.11 (67.23	6.34 6.48	9.79 9.91	11.18 11.04)
15b	0.5	**10b**	13								
		19	8	159-161	2527 1691	334	$C_{17}H_{22}N_2OS_2$	334.1174[a)] (334.1165)			
		20	9	97-99	1694	334	$C_{17}H_{22}N_2OS_2$	334.1174[a)] (334.1175)			
21a	0.83	**22a-i**	25	99-100	2580 1690	320	$C_{16}H_{20}N_2OS_2$	59.98 (60.04	6.30 6.33	8.75 8.63	19.98 19.80)
		22a-ii	23	130-132	2560 1695	320	$C_{16}H_{20}N_2OS_2$	59.98 (59.96	6.30 6.29	8.75 8.70	19.98 19.97)
21b	18.5	**22b**	12	187-188	2560 1695	334	$C_{17}H_{22}N_2OS_2$	61.06 (61.05	6.64 6.63	8.38 8.24	9.14 19.27)
		23	6	oil	1701	300	$C_{17}H_{20}N_2OS$	300.1296[a)] (300.1302)			
		24	9	oil	1725	318	$C_{17}H_{22}N_2O_2S$				

a Determined by HRMS spectrometry. Upper figure, calcd for M^+; lower figure, found.

Table 3. NMR Spectral Data for the Componds (**6-11**, **16-20**, and **22-24**)

Compd	^{1}H-NMR ($CDCl_3$, 400 MHz) δ	^{13}C-NMR ($CDCl_3$, 400 MHz) δ
6	1.39 (3H, s, CH_3), 1.58 (3H, s, CH_3), 1.9-2.2 (2H, m, $NCH_2C\underline{H}_2$-),	17.9(t), 24.3(q), 25.9(q), 30.2(t), 32.2(q), 41.3 (t),

Table 3. Continued

Compd	^{1}H-NMR ($CDCl_3$, 400 MHz) δ	^{13}C-NMR ($CDCl_3$, 400 MHz) δ
	2.75 (3H, s, NCH_3), 2.96 (1H, d, *J*= 9.7 Hz, S-CH_2-), 3.4-3.7 (2H, m, $NCH_2CH_2CH_2$-), 3.71 (1H, d, *J*= 9.7 Hz, SCH_2-), 4.5-4.9 (2H, m, NCH_2-), 6.9-7.2 (2H, m, ArH), 7.2-7.5 (3H, m, ArH)	42.2 (t), 44.4(s), 64.4(s), 88.4(s), 123.7(d) x2, 127.0(d), 128.8(d)x2, 145.3(s), 172.0(s), 172.3(s)
7b	1.50 (6H, s, CH_3x2), 1.8-2.1 (2H, m, NCH_2CH_2-), 2.61 (2H, t, *J*= 6.2 Hz, C=C-CH_2-), 2.64 (3H, s, NCH_3), 3.8-4.0 (2H, m, NCH_2-), 7.1-7.5 (5H, m, ArH)	21.2(q)x2, 22.0(t), 29.6(t), 36.3(q), 42.0(t), 47.5(s), 112.3(s), 127.6(d), 128.1(d)x2, 128.9(d)x2, 131.1 (s), 139.3(s), 169.6(s), 171.5(s)
8b	1.48 (6H, s, CH_3x2), 2.75-2.85 (2H, br t, C=C-CH_2-), 3.03 (3H, s, NCH_3), 3.9-4.0 (2H, br t, NCH_2-), 5.25(1H, d, *J*= 1.3 Hz, C=CH_2), 5.72 (1H, d, *J*= 1.3 Hz, C=CH_2), 7.2-7.5 (5H, m, ArH)	23.8(q)x2, 31.3(t), 32.6(q), 42.7(t), 46.2(s), 103.1 (s), 116.8(t), 126.5(d)x2, 127.8(d), 128.1(d)x2, 132.0(s), 139.4(s), 142.7(s), 168.0(s), 171.8(s)
7c	1.43 (6H, s, CH_3x2), 1.8-1.9 (2H, m, NCH_2CH_2-), 2.3-2.4 (2H, m, C=CH-CH_2-), 3.23 (3H, s, NCH_3), 3.8-3.9 (2H, m, NCH_2-), 4.69 (1H, t, *J*= 4 Hz, C=CH-CH_2-)	24.1(t), 22.1(t), 23.2(q)x2, 30.4(q), 41.1(t), 46.4 (s), 91.6(d), 133.9(s), 169.0(s), 169.6(s)
8c	1.46 (6H, s, CH_3x2), 2.8-2.9 (2H, m, C=C-CH_2-), 3.51 (3H, s, NCH_3), 3.90 (2H, t, *J*= 8.8 Hz, NCH_2-), 4.9-5.1 (2H, m, C=CH_2), 6.9-7.0 (1H, m, CH_2=CH-)	24.1(q)x2, 26.7(t), 33.1(q), 42.6(t), 45.9(s), 103.7 (s), 113.3(t), 128.9(d), 131.2(s), 167.9(s), 171.7(s)
9	1.17 (3H, s, CH_3), 1.55 (3H, s, CH_3), 1.71 (3H, s, CH_3), 1.8-2.0 (1H, m, NCH_2CH_2-), 2.0-2.1 (1H, m, NCH_2CH_2-), 2.71 (1H, d, *J*= 9 Hz, SCH_2-), 3.06 (1H, d, *J*= 9 Hz, SCH_2-), 3.50 (3H, s, NCH_3), 4.2-4.3 (1H, m, NCH_2-), 4.3-4.5 (1H, m, NCH_2-)	20.2(q), 20.6(q), 23.9(q), 30.7(t), 34.2(q), 37.8(t), 47.2(s), 51.1(t), 58.3(s), 80.7(s), 171.0 (s), 177.7(s)
10a	1.57 (6H, s, CH_3x2), 1.89 (3H, t, *J*= 1.5 Hz, C=C-CH_3), 2.5-2.6 (2H, br t, C=C-CH_2-), 3.59 (3H, s, NCH_3), 4.20 (2H, t, *J*= 8.3 Hz, NCH_2-)	14.4(q), 26.2(q)x2, 33.0(t), 34.2(q), 40.9(s), 52.0 (t), 121.8(s), 134.6(s), 170.7(s), 171.3(s)
10b	1.08 (6H, s, CH_3x2), 1.8-2.2 (2H, m, NCH_2CH_2-), 2.37 (2H, t, *J*= 6 Hz, C=C-CH_2-), 3.59 (3H, s, NCH_3), 4.49 (2H, br t, *J*= 5 Hz, NCH_2-), 7.0-7.5 (5H, m, ArH)	22.5(t), 25.4(q)x2, 35.0(t), 35.2(q), 44.7(s), 50.2(t), 127.2(d), 128.1(d)x2, 128.3(d)x2, 128.5 (s), 133.7 (s), 141.3(s), 171.4(s), 177.1(s)
10c	1.35 (6H, s, CH_3x2), 1.9-2.0 (2H, m, NCH_2CH_2-), 2.2-2.3 (2H, m, C=CH-CH_2-), 3.60 (3H, s, NCH_3), 4.3-4.4 (2H, m, NCH_2-), 5.27 (1H, t, *J*= 4 Hz, C=CH-CH_2-)	22.2(t), 23.2(t), 23.9(q)x2, 35.0(q), 42.3(s), 49.9(t), 110.2(d), 138.6(s), 171.2(s), 177.1(s)
11-i	1.19 (3H, s, CH_3), 1.39 (3H, s, CH_3), 1.96 (1H, s, SH), 2.0-2.3 (2H, m, NCH_2CH_2-), 3.2-3.3 (1H, m, C=C-CH-), 3.56 (3H, s, NCH_3), 3.7-3.8 (1H, m, NCH_2-), 4.1-4.2 (1H, m, NCH_2-), 5.2-5.4 (2H, m, C=CH_2), 5.9-6.1 (1H, m, CH_2=CH-)	19.7(q), 20.6(q), 27.5(t), 34.1(q), 48.3(s), 49.7 (d), 51.9(t), 77.6(s), 119.4(t), 135.6(d), 171.5(s), 176.8(s)
11-ii	1.04 (3H, s, CH_3), 1.26 (3H, s,CH_3), 1.7-1.9 (1H, m, NCH_2CH_2-), 2.1-2.2 (1H, m, NCH_2CH_2-), 2.9-3.0 (1H, m, C=C-CH-), 3.50 (3H, s, NCH_3), 3.6-3.8 (1H, m, NCH_2-), 4.1-4.3 (1H, m, NCH_2-), 5.1-5.3 (2H, m, C=CH_2), 5.6-5.8 (1H, m, CH_2=CH-)	
16a	1.50 (6H, s, CH_3x2), 2.97 (3H, s, NCH_3), 2.9-3.1 (2H, m, C=C-CH_2-), 3.97 (2H, br t, *J*= 8.5 Hz, NCH_2-), 7.2-7.4 (5H, m, ArH)	23.6(q)x2, 31.7(t), 33.6(q), 42.5(t), 46.4(s), 104.0(s), 127.4(d), 128.3(d)x2, 129.0(d)x2, 130.6(s), 134.9(s), 168.2(s), 172.2(s)
17	1.60 (6H, s, CH_3x2), 3.04 (3H, s, NCH_3), 6.30 (1H, d, *J*= 3.5 Hz, C=CH-), 7.15 (1H, d, *J*= 3.5 Hz, C=CH-), 7.2-7.4 (5H, m, ArH)	24.3(q)x2, 33.2(q), 48.0(s), 111.8(d), 112.2(s), 116.6(d), 127.5(d), 128.3(d)x2, 129.9(d)x2, 130.1(s), 134.5(s), 169.4(s), 170.5(s)
18a	1.33 (6H, s, CH_3x2), 2.8-2.9 (2H, m, C=C-CH_2-), 3.62 (3H, s, NCH_3), 4.3-4.5 (2H, m, NCH_2-), 7.1-7.2 (2H, m, ArH), 7.3-7.5 (3H, m, ArH)	26.7(q)x2, 34.3(q), 34.7(t), 41.6(s), 52.6(t), 126.3(s), 127.9(d), 128.5(d)x4, 135.8(s), 136.2(s), 171.1(s), 172.4(s)

Table 3. Continued

Compd	^{1}H-NMR ($CDCl_3$, 400 MHz) δ	^{13}C-NMR ($CDCl_3$, 400 MHz) δ
19	0.76 (3H, s, CH_3), 1.35 (3H, s, CH_3), 1.8-2.0 (2H, m, $NCH_2C\underline{H}_2$-), 2.0-2.2 (1H, m, $NCH_2CH_2C\underline{H}_2$-), 2.22 (1H, s, SH), 2.2-2.4 (1H, m, $NCH_2CH_2C\underline{H}_2$-), 3.3-3.5 (1H, m, PhCH-), 3.65 (3H, s, NCH_3), 4.3-4.5 (1H, m, NCH_2-), 4.7-4.9 (1H, m, NCH_2-), 7.2-7.4 (5H, m, ArH)	20.5(q), 20.7(q), 22.8(t), 29.8(t), 36.2(q), 47.3(d), 49.1(t), 50.1(s), 77.5(s), 127.9(d)x2, 128.8(d)x3, 141.6(s), 170.9(s), 181.4(s)
20	1.30 (3H, s, CH_3), 1.32 (3H, s, CH_3), 1.7-1.9 (1H, m, $NCH_2C\underline{H}_2$-), 2.1-2.2 (1H, m, $NCH_2CH_2C\underline{H}_2$-), 2.3-2.4 (1H, m, $NCH_2C\underline{H}_2$-), 2.4-2.6 (1H, m, $NCH_2CH_2C\underline{H}_2$-), 3.5-3.7 (1H, m, NCH_2-), 3.62 (3H, s, NCH_3), 4.11 (1H, dd, *J*= 10.3, 1.5 Hz, PhCH-), 4.76 (1H, s, SCH-), 5.1-5.2 (1H, m, NCH_2-), 7.2-7.4 (5H, m, ArH)	21.6(q), 24.2(q), 25.3(t), 34.7(q), 36.9(t), 42.2(s), 51.4(d), 53.6(t), 71.4(d), 127.3(d)x2, 127.8 (d), 128.8(d)x2, 141.4(s), 170.8(s), 179.8(s)
22a-i	1.34 (3H, s, CH_3), 1.9-2.1 (2H, m, $PhCHCH_2C\underline{H}_2$-), 2.1-2.3 (1H, m, $PhCHC\underline{H}_2$-), 2.17 (1H, s, SH), 2.9-3.0 (1H, m, $PhCHC\underline{H}_2$-), 3.28 (3H, s, NCH_3), 3.56 (1H, t, *J*= 10 Hz, PhCH-), 3.73 (3H, s, NCH_3), 7.2-7.3 (2H, m, ArH), 7.3-7.4 (3H, m, ArH)	20.3(q), 23.6(t), 31.7(t), 36.0(q), 44.1(q), 54.0(s), 54.9(d), 82.8(s), 128.5(d), 128.7(d)x2, 129.6(d)x2, 136.4(s), 171.2(s), 178.8(s)
22a-ii	1.42 (3H, s, CH_3), 2.0-2.2 (2H, m, $PhCHCH_2C\underline{H}_2$-), 2.2-2.4 (1H, m, $PhCHC\underline{H}_2$-), 2.54 (1H, s, SH), 3.0-3.1 (1H, m, $PhCHC\underline{H}_2$-), 3.25 (3H, s, NCH_3), 3.51 (3H, s, NCH_3), 3.5-3.6 (1H, m, PhCH-), 7.02 (2H, d, *J*=7.8 Hz, ArH), 7.2-7.3 (3H, m, ArH)	23.5(q), 27.0(t), 33.5(t), 35.3(q), 44.1(q), 52.6(s), 58.8(d), 83.9(s), 128.3(d)x2, 128.4(d) x3, 138.3(s), 170.7(s), 179.7(s)
22b	1.23 (3H, s, CH_3), 1.5-1.7 (1H, m, CH_3C-$C\underline{H}_2$-), 1.7-1.9 (2H, m, $PhCHCH_2C\underline{H}_2$-), 1.9-2.0 (1H, m, CH_3C-$C\underline{H}_2$-), 2.3-2.4 (1H, m, $PhCHC\underline{H}_2$-), 2.35 (1H, s, SH), 2.4-2.5 (1H, m, $PhCHC\underline{H}_2$-), 3.02 (3H, s, NCH_3), 3.2-3.4 (1H, m, PhCH-), 3.72 (3H, s, NCH_3), 7.1-7.2 (2H, m, ArH), 7.3-7.4 (3H, m, ArH)	22.3(q), 22.3(t), 28.3(t), 32.0(t), 35.4(q), 44.2(q), 49.3(s), 50.1(d), 81.0(s), 128.1(d), 128.6(d)x2, 129.5(d)x2, 138.8(s), 170.5(s), 179.2(s)
23	1.28 (3H, s, CH_3), 1.6-1.8 (1H, m, CH_3C-$C\underline{H}_2$-), 1.8-1.9 (1H, m, CH_3C-$C\underline{H}_2$-), 2.0-2.1 (2H, m, C=C-$CH_2C\underline{H}_2$-), 2.2-2.4 (1H, m, C=C-CH_2-), 2.6-2.8 (1H, m, C=C-CH_2-), 2.96 (3H, s, NCH_3), 3.57 (3H, s, NCH_3), 7.1-7.2 (2H, m, ArH), 7.2-7.4 (3H, m, ArH)	18.8(t), 22.4(q), 31.4(t), 31.6(t), 34.5(q), 42.8(s), 45.0(q), 128.0(d)x2, 128.1(d), 128.9(d)x2, 130.5(s), 134.5(s), 139.3(s), 172.5(s), 179.6(s)
24	0.9-1.9 (4H, m, $PhCH_2C\underline{H}_2C\underline{H}_2$-), 1.54 (3H, s, CH_3), 1.9-2.1 (2H, m, CH_3C-$C\underline{H}_2$-), 2.5-2.6 (2H, m, $PhCH_2$-), 3.65 (6H, s, NCH_3x2), 7.0-7.4 (5H, m, ArH)	

EXPERIMENTAL

All melting points were determined on a Yamato melting point apparatus (model MP-21) and are uncorrected. IR spectra were recorded on a JASCO A-102 spectrophotometer. NMR spectra were taken on JEOL-FX-90Q 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 HRMS spectra were recorded using a Micromass Auto Spec 3000 mass 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).

2,3-Dihydro-1,5,5-trimethyl-2-thioxo-4,6(1*H*,5*H*)-pyrimidinedione Triethylamine (11.1 mL, 80 mmol) was added to a mixture of dimethylmalonyl dichloride (5.2 mL, 40 mmol) and 1-methyl-2-thiourea (3.6 g, 40 mmol) in THF (250 mL) at rt. The reaction mixture was refluxed for 8 h, then poured into ice-water, acidified with 10% HCl, and extracted with AcOEt. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was recrystallized from AcOEt-hexane to give pale yellow prisms of 2,3-dihydro-1,5,5-trimethyl-2-thioxo-4,6(1*H*,5*H*)-pyrimidinedione (6.6 g, 89%), mp 151-152.5 °C. *Anal*. Calcd for $C_7H_{10}N_2O_2S$: C, 45.15; H, 5.41; N, 15.04; S, 17.22. Found: C, 45.21; H, 5.42; N, 15.11; S, 17.17.

2,3,4,5-Tetrahydro-1,5,5-trimethyl-2,6-dithioxo-4(1*H*)-pyrimidinone A solution of 2,3-dihydro-1,5,5-trimethyl-2-thioxo-4,6(1*H*,5*H*)-pyrimidinedione (6.0 g, 32 mmol) and Lawesson's reagent (7.5 g, 18 mmol) in xylene (55 mL) was reflux for 3 h. The solution was directly subjected to column chromatography on silica gel with $CHCl_3$ - hexane (1:2, v/v) to give 2,3,4,5-tetrahydro-1,5,5-trimethyl-2,6-dithioxo-4(1*H*)-pyrimidinone (4.23 g, 66%). Orange needles (from AcOEt-hexane), mp 159-160 °C. *Anal*. Calcd for $C_7H_{10}N_2OS_2$: C, 41.56; H, 4.98; N, 13.85; S, 31.70. Found: C, 41.62; H, 5.07; N, 14.04; S, 31.72.

2,3-Dihydro-1-(3-methyl-3-butenyl)-3,5,5-trimethyl-2-thioxo-4,6(1*H*,5*H*)-pyrimidinedione (4a) : Typical Procedure A solution of diethyl azodicarboxylate (2.09 g, 12 mmol) in THF (5 mL) was added dropwise under an N_2 atmosphere to a stirred mixture of 2,3-dihydro-1,5,5-trimethyl-2-thioxo-4,6(1*H*,5*H*)-pyrimidinedione (1.86 g, 10 mmol), 3-methyl-3-butene-1-ol (1.03 g , 12 mmol), and triphenylphosphine (3.12 g, 12 mmol) in THF (50 mL) at 0 °C. The reaction mixture was stirred at the same temperature for 4 h, then the solvent was evaporated *in vacuo*. The residue was chromatographed on silica gel with AcOEt-hexane (1:20, v/v) to give **4a** (1.94 g, 76%). Compounds (**4**, **5**, **14**, and **15**) were prepared from 2,3-dihydro-1,5,5-trimethyl-2-thioxo-4,6(1*H*,5*H*)-pyrimidinedione or 2,3,4,5-tetrahydro-1,5,5-trimethyl-2,6-dithioxo-4(1*H*)-pyrimidinone and the corresponding alcohols respectively, according to the procedure described above. The solvent systems used were as follows: **4b**, AcOEt-hexane (1:10, v/v); **14b**, **4c**, **5a**, **14a**, AcOEt-hexane (1:20, v/v); **5b, 5c, 15a, 15b**, AcOEt-hexane (1:30, v/v). Yields and analytical data of thiobarbiturates (**4,5,14,** and **15**) are listed in Table 1.

2,3,4,5-Tetrahydro-1,3,5-trimethyl-5-(3-phenylpropyl)-2,6-dithioxo-4(1*H*)-pyrimidinone (21a) i) Diethyl methylmalonate (4.35 g, 25 mmol) was added dropwise at 0 °C to a suspension of LiH (360 mg, 45 mmol) in DMF (30 mL) under an argon atmosphere, and the reaction mixture was stirred at the same temperature for 30 min. Then 3-phenylpropyl bromide (5.5 g, 28 mmol) was added dropwise to the above mixture at rt, and the mixture was stirred for an additional 3 h at 80 °C. The reaction mixture was poured into ice-water, acidified with 10% HCl, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was

chromatographed on silica gel with AcOEt-hexane (1:20, v/v) to give diethyl methyl(3-phenylpropyl)malonate (7.18 g, 98%), colorless oil. ^{1}H-NMR ($CDCl_3$, 90 MHz) δ: 1.22 (6H, t, *J*= 7 Hz, $C\underline{H}_3CH_2$ x 2), 1.39 (3H, s, CH_3), 1.4-2.0 (4H, m, $PhCH_2C\underline{H}_2C\underline{H}_2$-), 2.63 (2H, t, *J*= 7 Hz, $PhC\underline{H}_2$-), 4.16 (4H, q, *J*= 7 Hz, $CH_3C\underline{H}_2O$-x2), 7.0-7.5 (5H, m, ArH).

ii) A solution of KOH (4.17 g, 74 mmol) in H_2O (4.5 mL) was added at rt to a solution of diethyl methyl(3-phenylpropyl)malonate (7.18 g, 24.6 mmol) in EtOH (18 mL), and the reaction mixture was refluxed overnight. After removing the solvent, the residue was dissolved in H_2O, acidified with 10% HCl, and extracted with Et_2O. The organic layer was washed with brine and dried over $MgSO_4$, and evaporated to dryness. The residue was purified by recrystallization from AcOH-hexane to give methyl(3-phenylpropyl)methane-1,1-dicarboxylic acid (4.62 g, 80%), colorless needles, mp 131-133 °C. IR (Nujol): 2640, 1700 cm^{-1}.

iii) A mixture of the resulting dicarboxylic acid (3.54 g, 15 mmol) and phosphorus pentachloride (6.9 g, 33 mmol) in dry benzene (15 mL) was refluxed for 6 h. The reaction mixture was concentrated to yield the methyl (3-phenylpropyl)methane-1,1-dicarbonyl chloride, which was used for the next reaction without purification. Triethylamine (4.2 mL, 30 mmol) was added to a mixture of resulting dichloride (3.4 g, 12 mmol) and 1,3-dimethyl-2-thiourea (1.25 g, 12 mmol) in dry toluene (250 mL) at 50 °C. The reaction mixture was refluxed for 1 h, then poured into ice-water, acidified with 10% HCl, and extracted with AcOEt. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel with AcOEt-hexane (1:10, v/v) to give 2,3-dihydro-1,3,5-trimethyl-5-(3-phenylpropyl)-2-thioxo-4,6(1*H*, 5*H*)-pyrimidinedione (2.80 g, 77%). Pale yellow prisms, mp 73-74 °C (from diisopropyl ether-hexane). IR (Nujol): 1720, 1685 cm^{-1}. ^{1}H-NMR ($CDCl_3$, 90 MHz) δ: 1.1-1.7 (2H, m, $PhCH_2C\underline{H}_2$-), 1.53 (3H, s, CH_3), 1.9-2.2 (2H, m, $PhCH_2$-$CH_2C\underline{H}_2$-), 2.57 (2H, t, *J*= 7.5 Hz, $PhCH_2$-), 3.66 (6H, s, NCH_3 x 2), 7.0-7.4 (5H, m, ArH). MS (*m/z*): 304 (M^+).

iv) A solution of resulting 2,3-dihydro-1,3,5-trimethyl-5-(3-phenylpropyl)-2-thioxo-4,6(1*H*, 5*H*)-pyrimidinedione (1.3 g, 4.28 mmol) and Lawesson's reagent (2.0 g, 4.95 mmol) in xylene (10 mL) was refluxed for 2 days. The solution was directly subjected to column chromatography on silica gel with AcOEt-hexane (1:30, v/v) to give dithiobarbiturate (**21a** , 538 mg , 43%) along with corresponding trithiobarbiturate (134 mg, 9%) and unchanged monothiobarbiturate (452 mg, 35%).

2,3,4,5-Tetrahydro-1,3,5-trimethyl-5-(4-phenylbutyl)-2,6-dithioxo-4(1*H*)-pyrimidinone (21b) Compound (**21b**) was obtained by the same method as described for the preparation of **21a**, but with 4-phenylbutyl bromide in place of 3-phenylpropyl bromide.

Irradiation of Thiobarbiturate Derivatives (4,5,14,15, and 21): General Procedure A solution of thiobarbiturate (10 mM) in MeCN was irradiated with a 1 kW high-pressure mercury lamp through a Pyrex filter with water cooling. Progress of the reaction was monitored by TLC until the substrate disappeared. After removal of the solvent *in vacuo*, the residue was subjected to silica gel column chromatography. The solvent systems used were as follows: **4a**, AcOEt-hexane (3:2, v/v); **4b**,**21a**, AcOEt-hexane (1:6, v/v); **4c**, AcOEt-hexane (1:2, v/v); **5a,5b,5c,15a**, AcOEt-hexane (1:10,

v/v); **14a**,**14b**, AcOEt-hexane (1:1, v/v); **15b**, AcOEt-hexane (1:15, v/v); **21b**, AcOEt-hexane (1:20, v/v). Yields and analytical data of photoproducts of **4,5,14,15**, and **21** are listed in Table 2 and Table 3.

Thionation of 7b and 10b A solution of **7b** (40 mg, 0.14 mmol) and Lawesson's reagent (113 mg, 0.28 mmol) in xylene (2 mL) was reflux for 6 h. The solution was directly subjected to column chromatography on silica gel with AcOEt-hexane (1:10, v/v) to give **12** (44 mg, 100%). Yellow prisms, mp 146.5-147 ℃ (from diisopropyl ether-hexane). ^{1}H-NMR ($CDCl_3$, 90 MHz) δ: 1.77 (6H, s, CH_3x2), 1.9-2.3 (2H, m, $NC\underline{H}_2CH_2$-), 2.68 (2H, t, *J*= 6 Hz, C=C-CH_2-), 3.06 (3H, s, NCH_3), 4.3-4.5 (2H, m, NCH_2-), 7.2-7.5 (5H, m, ArH). MS (*m*/*z*): 316 (M^+).
Compound (**13**) was obtained by the same method as described for the preparation of **12**. Yield, 95%, yellow oil. ^{1}H-NMR ($CDCl_3$, 90 MHz) δ: 1.19 (6H, s, CH_3 x 2), 1.8-2.2 (2H, m, $NCH_2C\underline{H}_2$-), 2.2- 2.5 (2H, m, C=C-CH_2-), 4.10 (3H, s, NCH_3), 4.4-4.5 (2H, m, NCH_2-), 7.0-7.4 (5H, m, ArH). MS (*m*/*z*): 316 (M^+).

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