Photochemical Reactions of Pyrimidinethiones with Alkenes

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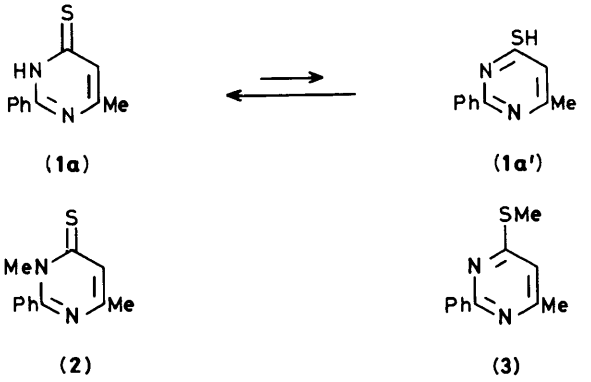
Photochemical addition reactions of pyrimidinethiones and related compounds with alkenes have been examined. Irradiation of pyrimidine-4(3*H*)-thiones (**1a**) in the presence of electron-poor alkenes gave the 4-mercaptoalkylated pyrimidines (**5**), whereas irradiation of (**1a**) in the presence of electron-rich alkenes gave 4-alkylthiopyrimidines (**6**). Irradiation of quinazoline-4(3*H*)-thiones (**1c—e**) and electron-poor alkenes gave 4-substituted quinazolines (**9**) and (**10**). This ready mode of carbon-carbon bond formation provides an efficient and novel method for alkylation of pyrimidine rings.

It has been demonstrated that a variety of thiones can undergo photochemical cycloaddition to various alkenes to give, as primary products, thietanes which are often unstable and are transformed into fragmentation products.[1] However, relatively few reports have dealt with the photochemical properties of thioimides[2] and thioamides.[3] It has recently been reported that thioamides undergo intramolecular[3f] or intermolecular[3h] photochemical cycloaddition with alkenes. Heteroaromatic thiones such as quinoxalinethiones,[4a] pyridinethiones,[4b,c] quinolinethiones,[4b] and pyridazinethiones[4d] also undergo photochemical cycloaddition with alkenes. Since in reactions, addition of the C=S group of thioamindes to carbon-carbon double bonds was unspecific,[3] it was thought that it might be possible to prepare 4- or 2-substituted pyrimidines and 4-substituted quinazolines by the photochemical reactions of pyrimidine-4(3*H*)-thiones, pyrimidine-2(1*H*)-thiones, and quinazoline-4(3*H*)-thiones with alkenes in a similar way. We now report the photochemical reactions of pyrimidine-4(3*H*)-thiones (**1a**, **b**), pyrimidine-2(1*H*)-thiones (**11**) and (**13**), quinazoline-4(3*H*)-thiones (**1c—e**), and related compounds (**15**) and (**17**) with alkenes (**4**), a useful method for the formation of C–C bonds.

Results and Discussion

Due to its ambident nature, two forms of *N*-unsubstituted pyrimidine-4(3*H*)-thione (**1**), either thione (**1a**) or thiol (**1a′**) are possible. The u.v. and ^{13}C n.m.r. spectra of 6-methyl-2-phenylpyrimidine-4(3*H*)-thione (**1a**) were compared with those of the *N*-methylated derivative, 3,6-dimethyl-2-phenylpyrimidine-4(3*H*)-thione (**2**) (thione form) and the *S*-methylated derivative, 4-methylthio-6-methyl-2-phenylpyrimidine (**3**) (thiol form). The u.v. spectrum of compound (**1a**) in various solvents was similar to that of (**2**), but different to that of compound (**3**)

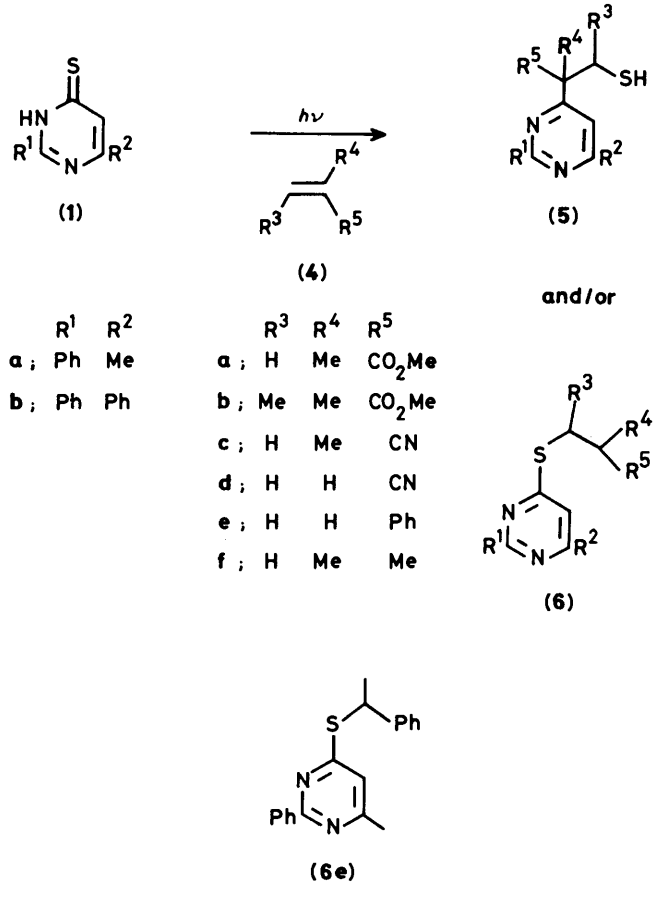


(Table 1). The ^{13}C n.m.r. spectrum of (**1a**) gave a singlet at δ 182.6 assignable to thiocarbonyl carbon at C-4 but the carbon peak due to the thiol form around δ 170 was not observed, while the spectra of (**2**) and (**3**) gave singlet at δ 185.9 and 169.8 due to the thiocarbonyl carbon at C-4 of (**2**) and the pyrimidine ring carbon at C-4 adjacent to the methylthio group of (**3**) respectively. These facts suggested that the pyrimidine-4(3*H*)-thione (**1a**) exists predominantly as the thione form in solution. Irradiation of a solution of 6-methyl-2-phenylpyrimidine-4(3*H*)-thione (**1a**) in benzene in the presence of methyl methacrylate (**4a**) in a Pyrex vessel with a high-pressure mercury lamp under argon at room temperature for 8 h until yellow colour of the solution disappeared, gave a 1:1-adduct of (**1a**) and (**4a**) in 66% yield after purification by column chromatography. The structure of (**5a**) was confirmed on the basis of spectroscopic properties and elemental analysis. Thiol and ester carbonyl absorptions in the i.r. spectrum appeared at 2 590 and 1 725 cm^{-1}, respectively. The ^1H n.m.r. spectrum of (**5a**) gave signals at δ 1.42 (1 H, t, SH), 1.72 (3 H, s, Me), 2.58 (3 H, s, Me), 3.29 (2 H,

Table 1. U.v. and ^{13}C n.m.r. spectra of 6-methyl-2-phenylpyrimidine-4(3*H*)-thione (**1a**), 3,6-dimethyl-2-phenylpyrimidine-4(3*H*)-thione (**2**), and 4-methylthio-6-methyl-2-phenylpyrimidine (**3**)

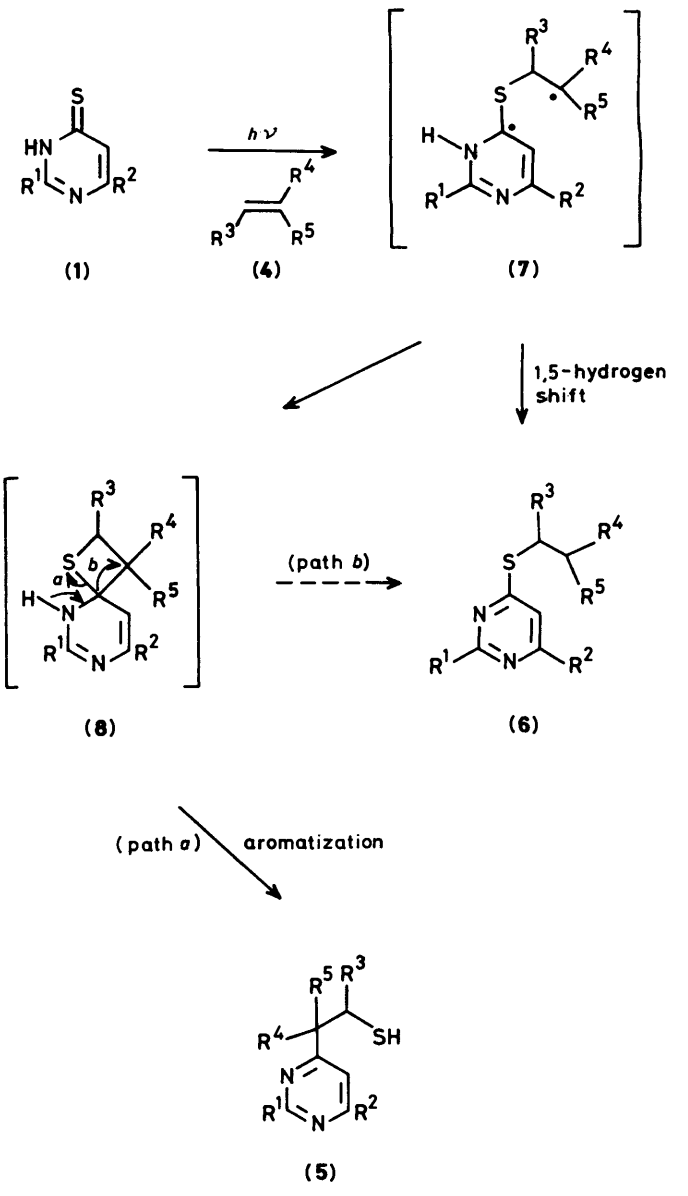
Compound	Solvent	$\lambda_{max.}$/nm (ε × 10^3)	δ_C at C-4 ($CDCl_3$)
(**1a**)	EtOH	243 (13.7), 250.5 (13.9), 306 (16.4), 351 (6.6)	182.6
(**1a**)	THF	249 (14.1), 283sh (6.5), 311 (18.2), 365 (5.6)	
(**1a**)	$CHCl_3$	255.5 (16.3), 307.5 (11.7), 359 (4.9)	
(**2**)	EtOH	232sh (10.0), 299.5 (15.6), 336 (7.5)	185.9
(**2**)	THF	238sh (9.3), 286sh (11.6), 301 (16.9), 344 (6.9)	
(**2**)	$CHCl_3$	241sh (9.3), 301 (15.8), 339 (8.3)	
(**3**)	EtOH	253.5 (29.5)	169.8
(**3**)	THF	253.5 (14.4)	
(**3**)	$CHCl_3$	255.5 (30.1)	

d, CH_2), and 3.73 (3 H, s, CO_2Me) in addition to signals due to aromatic protons. ^{13}C N.m.r. signals at δ_C 21.3 (q), 24.6 (q), 52.5 (q), 32.3 (t), 55.0 (s), and 173.8 p.p.m. (s) due to two methyl, methoxy, methylene, quatenary, and carbonyl carbons, respectively, in addition to aromatic carbon signals were present. Thus, the photoproduct was characterized as the 4-mercaptoalkylated pyrimidine (**5a**). Similarly, irradiation of pyrimidine-4(3*H*)-thiones (**1a**, **b**) in the presence of electron-poor alkenes such as methyl 2-methylbut-2-enoate (**4b**), methacrylonitrile (**4c**), and acrylonitrile (**4d**) under the same conditions gave 4-mercaptoalkylated pyrimidines (**5b**—**d**) in moderate yields. Irradiation of a solution of thione (**1a**) and the electron-neutral alkene, styrene (**4e**), in benzene gave 4-mercaptoalkylated pyrimidine (**5e**) and 4-alkylthiopyrimidine (**6e**) (anti-Markownikoff type addition product) in 10 and 59% yields, respectively (Scheme 1).



Scheme 1.

A solution of compounds (**1a**) and (**4e**) in benzene was heated to reflux to yield another 4-alkylthiopyrimidine (**6e'**) (Markownikoff type addition product) in 60% yield, suggesting that (**6e**) is produced in the photoreaction. On the other hand, irradiation of (**1a**) and electron-rich alkenes such as isobutene (**4f**) under the same conditions gave 4-alkylthiopyrimidines (**6f**—**g**) as the sole products in 90% yield. However, irradiation of *N*-alkylated pyrimidine-4(3*H*)-thione (**2**) in the presence of electron-poor alkenes such as methyl methacrylate (**4a**) and methacrylonitrile (**4c**) gave no photoproducts and thione (**2**) was completely recovered. When a solution of (**1a**) and (**4a**) in benzene in the presence of triplet sensitizer, Michler's ketone (E_T = 62 kcal mol^{-1}) was irradiated, the yield of the pyrimidine (**5a**) was quite low (<5%) and more than 95% of starting



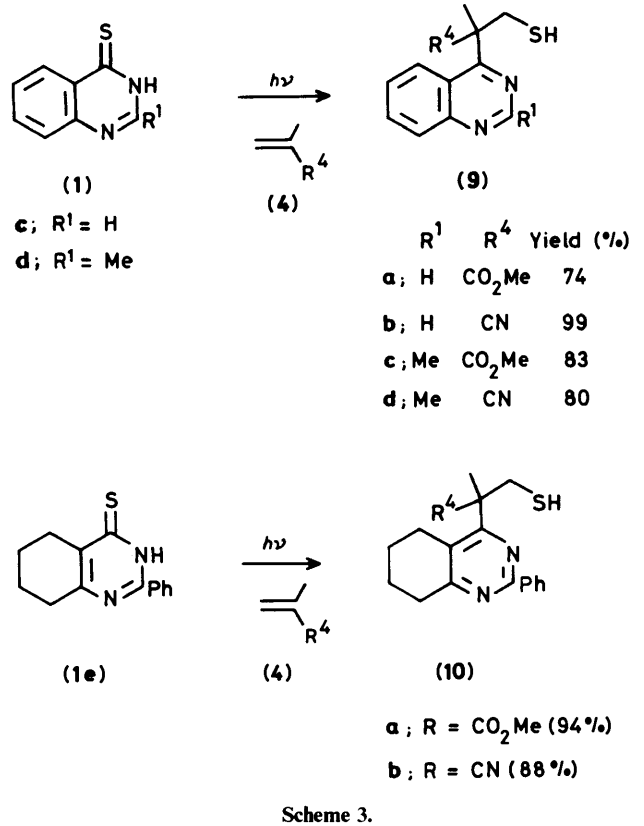
Scheme 2.

pyrimidine-4(3*H*)-thione (**1a**) was recovered. The formation of (**5a**) was not quenched by the addition of cyclo-octatetraene[5] as a triplet quencher in this reaction system. The 4-mercaptoalkylated pyrimidine (**5a**) was also produced in 43% yield when compound (**1a**) was irradiated in the presence of methyl methacrylate (**4a**) in the n, π^* region of thioamide groups with halogen lamp (>400 nm) (See Table 2). These results suggest that the formation of 4-mercaptoalkylated pyrimidine (**5a**) occurs from n,π^* singlet state of (**1a**). The most plausible mechanism for the formation of 4-mercaptoalkylated pyrimidines (**5**) and 4-alkylthiopyrimidine (**6**) is presented in Scheme 2. The pyrimidine-4(3*H*)-thione (**1**) reacted with alkene (**2**) to form the 1,4-diradical (**7**), which gave the 4-alkylthiopyrimidine (**4**) by 1,5-hydrogen transfer[5–7] or the thietane (**8**) by recombination of the 1,4-diradical. The latter underwent ring cleavage with aromatization of the pyrimidine ring to yield the 4-mercaptoalkylated pyrimidine (**5**) (path *a*). A somewhat similar hydrogen transfer reaction has been reported by de Mayo and co-workers,[5] Ohno *et al.*,[6] and Brouwer and Bos.[7] The alkylthiopyrimidine (**6**) might be also formed by the ring

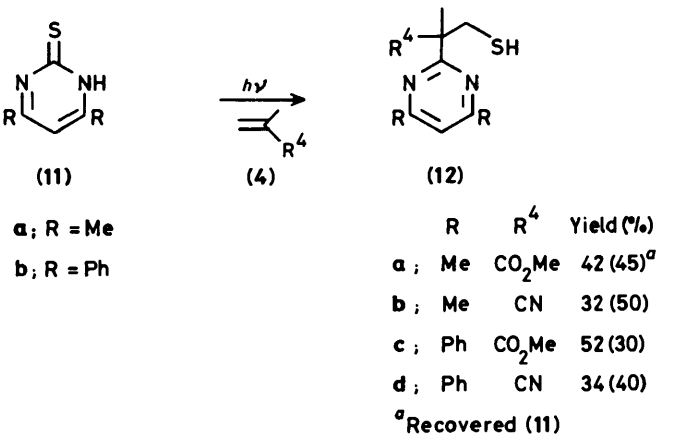
Table 2. The yield of photoproducts (**5**) and (**6**)

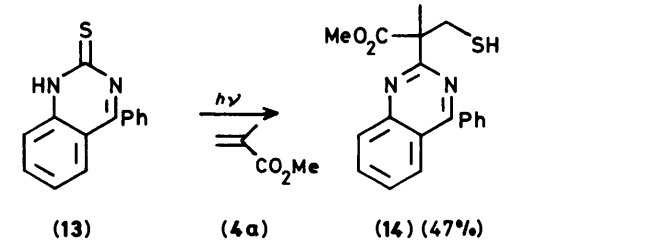
Run	Pyrimidinethione	Alkene	Product (yield, %)[a]			
1	(**1a**)	(**4a**)	(**5a**)	(66)		
2[b]	(**1a**)	(**4a**)	(**5a**)	(35)		
3[b,c]	(**1a**)	(**4a**)	(**5a**)	(<5)		
4[d]	(**1a**)	(**4a**)	(**5a**)	(48)		
5[e]	(**1a**)	(**4a**)	(**5a**)	(42)		
6	(**1a**)	(**4b**)	(**5b**)	(58)		
7	(**1a**)	(**4c**)	(**5c**)	(60)		
8	(**1a**)	(**4d**)	(**5d**)	(34)		
9	(**1a**)	(**4e**)	(**5e**)	(10)	(**6e**)	(59)
10	(**1a**)	(**4f**)			(**6f**)	(90)
11	(**1b**)	(**4a**)	(**5j**)	(84)		
12	(**1b**)	(**4b**)	(**5k**)	(76)		

[a] Isolated yield. [b] Irradiation was carried out at 366 nm light. A Pyrex filter and methanol solution of naphthalene (5 g l^{-1}) were used to isolate the 366 nm region. [c] Irradiation was carried out in the presence of Michler's ketone as a triplet sensitizer, which absorbs more than 95% of the incident light. [d] Irradiation was carried out in the presence of cyclooctatetraene (2.5 mol equiv.) as a triplet quencher. [e] A halogen lamp was used as an irradiation source.

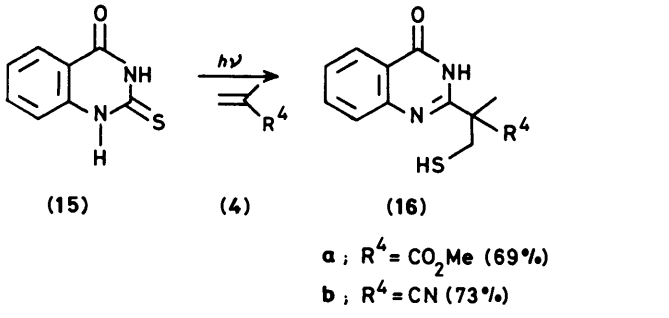


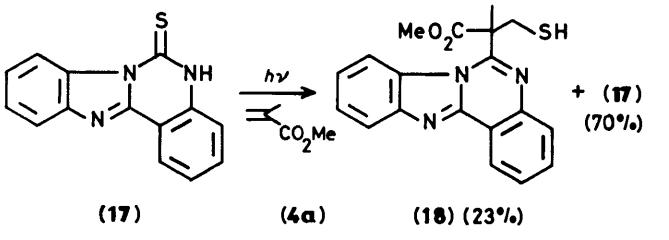
Scheme 3.





Scheme 4.





Scheme 5.

cleavage of thietane (path *b*); however, this is unlikely because the bond energy of C–C bonds (83 kcal mol^{-1}) is stronger than that of C–S bonds (42—44 kcal mol^{-1}). The regiochemistry of addition of thioamide (**1**) to alkene (**4**) is in accord with previously published works on thioamide photochemistry.[3a–c,4] The regiospecificity is that expected with the formation of more stable possible diradical intermediate (**7**). The difference in photochemical behaviour of the pyrimidine-4(3*H*)-thione (**1a**) compared to electron-poor or rich alkenes cannot be explained at present.* Irradiation of the quinazoline-4(3*H*)-thiones (**1c**—**e**) in dimethoxyethane (DME) in the presence of electron-poor alkenes (**4a, c**) gave the 4-mercaptoalkylated quinazolines (**9a**—**d**, **10a**—**b**) in high yields. The formation of compounds (**9**) and (**10**) can be also explained through the intermediacy of an unstable thietane, formed initially by the photochemical [2 + 2]cycloaddition of thiocarbonyl to alkene, which undergoes ring cleavage with aromatization of the quinazoline ring to yield the final products (Scheme 3).

The pyrimidine-2(1-*H*)-thiones (**11**) and (**13**) also reacted

* One of the referees suggested the possibility of an electron transfer mechanism in the case of electron-poor alkenes.

photochemically with electron-poor alkenes (**4a**, **c**) to yield the corresponding mercaptoalkylated pyrimidines (**12**) and (**14**) respectively (Scheme 4). Photochemical reactions of 2-thioxoquinazolin-4(3*H*)-one (**15**) and benzimidazo[1,2-*c*]quinazoline-6-thiol (**17**) were studied in relation to those of the pyrimidinethiones (**1**), (**11**), and (**13**). Photolysis of (**15**) in DME in the presence of electron-poor alkenes (**4a**, **b**) yielded 2-mercaptoalkylated quinazolin-4(3*H*)-ones (**16a**, **b**) in 69—73% yields. Irradiation of a solution of the thiol (**17**) and methyl methacrylate (**4a**) in DME afforded 6-mercaptoalkylated benzoimidazo[1,2-*c*]quinazoline (**18**) (Scheme 5). The structure of the photoproducts (**16**) and (**18**) was confirmed on the basis of spectroscopic properties and elemental analyses. The ready mode of C–C bond formation described here, therefore provides an efficient and novel method for the preparation of 4- or 2-substituted pyrimidines (**5**), (**9**), (**10**), (**12**), and (**14**).

Experimental

M.p.s and b.p.s were measured with a Yanaco micro-melting point apparatus (MP-J3) and Büchi Kugelrohr distillation apparatus (KR-3), respectively and are uncorrected. U.v. spectra were recorded on Shimadzu UV-365 or JASCO UVIDEC-505 spectrophotometers. I.r. spectra were determined with JASCO IRA-1 or Hitachi 260-30 spectrophotometers. ^1H and ^{13}C n.m.r. spectra were run on JEOL FX-100 (100 MHz) or FX-90Q (90 MHz) spectrometers using tetramethylsilane as an internal standard. Silica gel (Merck Kieselgel 60 or Wakogel C-300 for flash chromatography) was used for column chromatography.

Starting Materials.—The pyrimidine-2(1*H*)-thione (**11a**) was obtained from Tokyo Kasei Kogyo Co. and 2-thioxoquinazolin-4(3*H*)-one (**15**) and benzimidazo[1,2-*c*]quinazoline-6-thione (**17**) from the Aldrich Chemical Co. Pyrimidine-4(3*H*)-thiones (**1a**, **b**), quinazoline-4(3*H*)-thiones (**1c**—**e**), pyrimidine-2(1*H*)-thione (**11b**), and quinazoline-2(1*H*)-thione (**13**) were prepared from the corresponding keto forms following the procedure of Lawesson et al.[8] The compounds thus obtained were purified through silica gel column chromatography (eluant: benzene–ethyl acetate 50:1—4:1) and further recrystallized from chloroform–hexane.

6-Methyl-2-phenylpyrimidine-4(3*H*)-thione (**1a**), (67%), m.p. 187—188 °C (Found: C, 65.0; H, 4.95; N, 13.85. $C_{11}H_{10}N_2S$ requires C, 65.3; H, 5.0; N, 13.85%); $\nu_{max.}$(KBr) 1 600, 1 580, 1 540, 1 250, 1 125, 785, 740, and 695 cm^{-1}; $\delta_H(CDCl_2)$ 2.37 (3 H, s, Me), 7.15 (1 H, s, =CH), 7.41—7.67 (3 H, m, Ph), 7.88—8.07 (2 H, m, Ph), and 10.9 (1 H, br s, NH); $\delta_C(CDCl_3)$ 23.8 (q, Me), 124.4 (d), 127.8 (d) 129.1 (d), 130.9 (s), 132.5 (d) (ArC and =C–), 156.5 [s, =C(Me)–], 162.3 (s, C=N), and 182.4 (s, C=S).

2,6-Diphenylpyrimidine-4(3*H*)-thione (**1b**), (58%), m.p. 213—215 °C (Found: C, 72.5; H, 4.6; N, 10.55. $C_{16}H_{12}N_2S$ requires C, 72.7; H, 4.55; N, 10.6%); $\lambda_{max.}$(EtOH) 238 (ε 1.49 × 10^4 dm^3 mol^{-1} cm^{-1}), 267sh (1.73 × 10^4), 299 (3.21 × 10^4), and 408 nm (2.7 × 10^3); $\nu_{max.}$(KBr) 3 150, 1 585, 1 570, 1 265, 1 145, 765, 735, and 680 cm^{-1}; $\delta_H(CDCl_3)$ 7.26 (1 H, s, =CH), 7.47—7.74 (6 H, m, Ph), and 8.08—8.18 (4 H, m, Ph).

Quinazoline-4(3*H*)-thione (**1c**), (~100%), m.p. 290 °C (sublimation) (Found: C, 59.25; H, 3.7; N, 17.45. $C_8H_6N_2S$ requires C, 59.25; H, 3.7; N, 17.25%); $\nu_{max.}$(KBr) 3 140, 1 615, 1 590, 1 560, 1 249, 1 195, 805, 760, and 755 cm^{-1}; δ_H([$^2H_6$]DMSO) 7.56—8.40 (4 H, m, ArH), 8.64—8.75 (1 H, m, –CH=N–), and 13.9 (1 H, br s, NH).

2-Methylquinazoline-4(3*H*)-thione (**1d**), (95%), m.p. 220—222 °C (Found: C, 61.5; H, 4.65; N, 16.1. $C_9H_8N_2S$ requires C, 61.35; H, 4.55; N, 15.9%); $\nu_{max.}$(KBr) 3 150, 1 625, 1 578, 1 245, 840, and 765 cm^{-1}; δ_H ([$^2H_6$]DMSO) 2.57 (3 H, s, Me), 3.89 (1 H, br s, NH), 7.35—8.01 (3 H, m, ArH), and 8.63 (1 H, dd, *J* 1.0, 7.7 Hz, ArH); δ_C([$^2H_6$]DMSO) 21.2 (q, Me), 127.4 (d), 129.2 (d), 144.7 (s) (ArC), 153.0 (s, C=N), and 186.9 (s, C=S).

2-Phenyl-5,6,7,8-tetrahydroquinazoline-4(3*H*)-thione (**1e**), (81%), m.p. 195.5—197 °C (Found: C, 69.55; H, 5.75; N, 11.45. $C_{14}H_{14}N_2S$ requires C, 69.4; H, 5.9; N, 11.55%); $\nu_{max.}$(KBr) 3 150, 1 565, 1 245, 1 210, 785, 740, and 700 cm^{-1}; δ_H([$^2H_6$]-DMSO) 1.8—2.0 (4 H, m), 2.5—2.9 (4 H, m), (CH_2), 3.91 (1 H, br s, NH), 7.51—7.80 (3 H, m, Ph), and 8.12—8.25 (2 H, m, Ph); δ_C([$^2H_6$]DMSO) 21.8 (t), 21.9 (t), 26.8 (t), 31.9 (t) (CH_2), 128.3 (d), 128.6 (d), 131.1 (s), 131.6 (d) (ArC), 153.6 (s, C=C), 158.5 (s, C=N), and 183.8 (s, C=S).

4,6-Diphenylpyrimidine-2(1*H*)-thione (**11b**), (80%), m.p. 222—224 °C (Found: C, 72.35; H, 4.6; N, 10.55. $C_{16}H_{12}N_2S$ requires C, 72.7; H, 4.55; N, 10.6%); $\nu_{max.}$(KBr) 3 130, 1 600, 1 540, 1 225, 770, 745, and 695 cm^{-1}; δ_H([$^2H_6$]DMSO) 7.55—7.93 (7 H, m, Ph and =CH–), and 8.19—8.29 (4 H, m, Ph).

4-Phenylquinazoline-2(1*H*)-thione (**13**), (81%), m.p. 205—206 °C (Found: C, 70.7; H, 4.15; N, 11.6. $C_{14}H_{10}N_2S$ requires C, 70.55; N, 4.2; N, 11.75%); $\nu_{max.}$(KBr) 1 610, 1 550, 1 270, 1 215, 760, and 700 cm^{-1}; δ_H([$^2H_6$]DMSO) 7.22—8.00 (9 H, m, Ph) and 14.0 (1 H, br s, NH); δ_C([$^2H_6$]DMSO) 115.9 (d), 124.8 (d), 128.1 (d), 128.6 (d), 129.6 (d), 130.8 (d), 135.9 (s), 135.9 (d), 142.5 (s), (ArC), 168.3 (s, C=N), and 180.8 (s, C=S).

Preparation of 3,6-*Dimethyl*-2-*phenylpyrimidine*-4(3H)-*thione* (**2**).—A solution of 3,6-dimethyl-2-phenylpyrimidine-4(3*H*)-one[9] (1.1 g) and Lawesson's reagent (1.22 g) in dry benzene (50 ml) was refluxed for 10 h. After evaporation of the solvent under reduced pressure, the residue was chromatographed on a silica gel column with chloroform–methanol (15:1) to give the thione (**15**) in 84% yield, m.p. 107.5—108.5 °C (Found: C, 66.6; H, 5.6; N, 12.9. $C_{12}H_{12}N_2S$ requires C, 66.65; H, 5.6; N, 12.95%); $\nu_{max.}$(KBr) 1 585, 1 505, 1 290, 1 145, 775, and 690 cm^{-1}; $\delta_H(CDCl_3)$ 2.31 (3 H, s, Me), 3.83 (3 H, s, NMe), 7.41 (1 H, s, =C–), and 7.53 (5 H, s, Ph); $\delta_C(CDCl_3)$ 22.9 (q, Me), 41.9 (q, NMe), 126.9 (d), 127.9 (d), 129.0 (d), 130.6 (d), 134.9 (s) (ArC and =C–), 156.7 [s, =C(Me)–], 160.2 (s, C=N), and 185.9 (s, C=S).

Preparation of 4-*Methylthio*-6-*Methyl*-2-*phenylpyrimidine* (**3**).—A solution of the pyrimidine-4(3*H*)-thione (**1a**) (1.1 g), methyl iodide (710 mg), and potassium carbonate (828 mg) in acetone (30 ml) was heated at 60 °C for 15 h in a sealed tube. After being cooled, the reaction mixture was poured into water and then extracted with methylene dichloride. The extract was washed with 10% hydrochloric acid and then dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–hexane (6:1) to yield the pyrimidine (**16**) (99%), b.p. 112 °C at 4 mmHg (Found: C, 66.85; H, 5.7; N, 12.9. $C_{12}H_{12}N_2S$ requires C, 66.65; H, 5.6; N, 12.95%); $\nu_{max.}$($CHCl_3$) 1 585, 1 560, 1 515, 1 300, 1 140, 1 110, 825, 745, and 690 cm^{-1}; $\delta_H(CDCl_3)$ 2.42 (3 H, s, Me), 2.60 (3 H, s, SMe), 6.82 (1 H, s, =CH–), 7.35—7.46 (3 H, m, Ph), and 8.36—8.50 (2 H, m, Ph); $\delta_C(CDCl_3)$ 12.2 (q, Me), 23.9 (q, SMe), 128.2 (d), 130.5 (d), 137.7 (s) (ArC), 115.4 (d), 163.2 (s), 164.4 (s), and 169.8 (s), (pyrimidine ring C).

General Procedure for the Photochemical Reactions of Pyrimidinethiones (**1**), (**11**), (**13**), and (**17**) *with Alkenes* (**4**).—A solution of pyrimidinethione (200 mg) and a large excess of alkene (*ca.* 1 ml) in dry benzene [70 ml, for pyrimidine-4(3*H*)-thiones (**1a**, **b**)] or DME [70 ml, for the other pyrimidinethiones (**1c**—**e**), (**11**), (**13**), (**15**), and (**17**)] in a Pyrex vessel was irradiated with a high-pressure mercury lamp (300 or 450 W) under argon for 2—15 h until the colour of the solution had disappeared at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (50:1—4:1) as eluant to yield the

photoproducts, along with a small amount of starting thiones [except (**11a,b**) and (**17**), see Schemes 4 and 5].

Mercaptoalkylated pyrimidine (**5a**), b.p. 160 °C at 2 mmHg (Found: C, 63.85; H, 6.0; N, 9.5. $C_{16}H_{18}N_2O_2S$ requires C, 63.55; H, 6.0; N, 9.25%); $\nu_{max.}$($CHCl_3$) 2 590, 1 725, 1 585, 1 570, 1 365, 1 220, 1 130, and 1 110 cm^{-1}; δ_H($CDCl_3$) 1.42 (1 H, t, *J* 9.3 Hz, SH), 1.72 (3 H, s, Me), 2.58 (3 H, s, Me), 3.29 (2 H, d, *J* 9.3 Hz, CH_2), 3.73 (3 H, s, CO_2Me), 7.01 (1 H, s, =CH–), 7.43—7.53 (3 H, m, Ph), and 8.40—8.50 (2 H, m, Ph); δ_C($CDCl_3$) 21.3 (q, Me), 24.6 (q, Me), 32.3 (t, CH_2), 52.5 (q, CO_2Me), 55.0 (quaternary C), 128.3 (d), 128.4 (d), 130.6 (d), 137.6 (s) (ArC), 115.7 (d), 163.7 (s), 167.7 (s), 169.1 (s) (pyrimidine ring C), and 173.8 (s, CO_2).

Mercaptoalkylated pyrimidine (**5b**), b.p. 175 °C at 2 mmHg (Found: C, 64.25; H, 6.2; N, 8.65. $C_{17}H_{20}N_2O_2S$ requires C, 64.55; H, 6.35; N, 8.85%); $\nu_{max.}$($CHCl_3$) 1 715, 1 575, 1 545, 1 360, 1 240, and 1 190 cm^{-1}; δ_H($CDCl_3$) 1.40 (3 H, d, *J* 7.3 Hz, Me), 1.50 (1 H, d, *J* 6.8 Hz, SH), 1.72 (3 H, s, Me), 2.56 (3 H, s), 3.66 (3 H, d, CO_2Me), 4.05—4.35 (1 H, m, CH), 7.06 (1 H, s, =CH–), 7.32—7.57 (3 H, Ph), and 8.44—8.54 (2 H, m, Ph); δ_C($CDCl_3$) 16.7 (q, Me), 21.0 (q, Me), 24.5 (q, Me), 40.4 (d, CH), 52.3 (q, CO_2Me), 58.0 (s, quaternary C), 128.2 (d), 130.5 (d), 137.6 (s), (ArC), 116.0 (d), 163.7 (s), 167.4 (s), 168.8 (s) (pyrimidine ring C), and 173.2 (s, CO_2).

Mercaptoalkylated pyrimidine (**5c**), m.p. 88—88.5 °C, (Found: C, 66.75; H, 5.6; N, 15.55. $C_{15}H_{15}N_3S$ requires C, 66.9; H, 5.6; N, 15.6%); $\nu_{max.}$(KBr) 2 570, 2 330, 1 585, 1 570, 1 540, 1 370, 760, and 700 cm^{-1}; δ_H($CDCl_3$) 1.64 (1 H, X of ABX, *J* 9.3 Hz, SH), 1.81 (3 H, s, Me), 2.62 (3 H, s, Me), 3.05 (1 H, A of ABX, *J* 9.3, 14.2 Hz), 3.37 (1 H, B of ABX, *J* 9.3, 14.2 Hz) (CH_2), 7.23—7.50 (4 H, m, =CH– and Ph), and 8.40—8.50 (2 H, m, Ph), δ_H($CDCl_3$) 2.45 (q, Me), 25.4 (q, Me), 33.5 (t, CH_2), 47.7 (s, quaternary C), 120.9 (s, CN), 128.2 (d), 128.4 (d), 130.9 (d), 136.9 (s), (ArC), 115.8 (d), 164.2 (s), 165.1 (s), and 168.9 (s) (pyrimidine ring C).

Mercaptoalkylated pyrimidine (**5d**), m.p. 77—78 °C (Found: C, 65.65; H, 5.1; N, 16.45. $C_{14}H_{13}N_3S$ requires C, 65.85; H, 5.15; N, 16.45%); $\nu_{max.}$(KBr) 2 230, 1 585, 1 560, 1 365, 745, and 695 cm^{-1}; δ_H($CDCl_3$) 1.78 (1 H, t, *J* 9.8 Hz, SH), 2.61 (3 H, s, Me), 3.24 (2 H, dd, *J* 5.9, 9.3 Hz, CH_2), 4.22 (1 H, t, *J* 5.9 Hz, CH), 7.23 (1 H, s, =CH–), 7.34—7.51 (3 H, m, Ph), and 8.29—8.53 (2 H, m, Ph); δ_C($CDCl_3$) 24.5 (q, Me), 26.9 (t, CH_2), 43.1 (d, CH), 117.9 (s, CN), 128.2 (d), 128.5 (d), 130.0 (d), 136.7 (s) (ArC), 116.7 (d), 160.8 (s), 164.4 (s), and 168.9 (s) (pyrimidine ring C).

The mercaptoalkylated pyrimidine (**5e**) and the alkylthiopyrimidine (**6e**) were not completely separated. Their structures were elucidated on the basis of their n.m.r. spectra: b.p. [mixture of (**5e**) and (**6e**)] 150—160 °C at 4 mmHg (Found [for a mixture of (**5e**) and (**6e**)]: C, 74.25; H, 5.95; N, 9.20. $C_{19}H_{18}N_2S$ requires C, 74.45; H, 5.9; N, 9.15%); (**5e**), δ_H($CDCl_3$) 2.46 (3 H, s, Me), 3.57—3.79 (2 H, m, CH_2), 4.12 (1 H, dd, *J* 6.8, 8.3 Hz, CH), 6.81 (1 H, =CH–), 7.12—7.67 (8 H, m, Ph), and 8.39—8.59 (2 H, m, Ph); δ_C($CDCl_3$) 24.2 (q, Me), 28.8 (t, CH_2), 56.8 (d, CH), 118.3 (d), 163.3 (s), 164.6 (s), and 167.2 (s) (pyrimidine ring C) in addition to aromatic carbon peaks. (**6e**), δ_H($CDCl_3$) 2.43 (3 H, s, Me), 2.97—3.59 (4 H, A_2B_2 m, $-CH_2CH_2-$), 6.85 (1 H, s, =CH–), 7.16—7.67 (8 H, m, Ph), and 8.39—8.58 (2 H, m, Ph); δ_C($CDCl_3$) 24.0 (q, Me), 30.5 (t), 36.0 (t) (CH_2), 126.5 (d), 128.3 (d), 128.5 (d), 128.6 (d), 128.8 (d), 130.5 (d), 137.7 (s), 140.2 (s) (ArC), 116.1 (d), 163.3 (s), 164.6 (s), 169.0 (s) (pyrimidine ring C).

Mercaptoalkylated pyrimidine (**5j**), b.p. 185 °C at 2 mmHg (Found: C, 69.45; H, 5.65; N, 7.55. $C_{21}H_{20}N_2OS$ requires C, 69.2; H, 5.55; N, 7.7%); $\nu_{max.}$(film) 2 580, 1 735, 1 590, 1 565, 1 535, 1 375, 1 285, 1 235, 1 105, 755, and 695 cm^{-1}; δ_H($CDCl_3$) 1.48 (1 H, t, *J* 8.8 Hz, SH), 1.79 (3 H, s, Me), 3.55 (2 H, d, *J* 8.8 Hz, CH_2), 3.73 (3 H, s, CO_2Me), 7.31 (1 H, s, =CH–), 7.40—7.60 (6 H, m, Ph), 8.12—8.24 (2 H, m, Ph), and 8.55—8.66 (2 H, m, Ph); δ_C($CDCl_3$) 21.3 (q, Me), 32.3 (t, CH_2), 52.4 (q, CO_2CH_3), 55.2 (s, quaternary C), 127.2 (d), 128.3 (d), 128.7 (d), 130.6 (d), 130.7 (d), 137.0 (s), 137.5 (s) (ArC), 111.7 (d), 163.7 (s), 164.4 (s), 169.9 (s) (pyrimidine ring C), and 173.6 (s, CO_2)

Mercaptoalkylated pyrimidine (**5k**), b.p. >250 °C at 2 mmHg (Found: C, 72.85; H, 5.15; N, 12.9. $C_{20}H_{17}N_3S$ requires C, 72.45; H, 5.15; N, 12.65%); $\nu_{max.}$(film) 2 570, 2 245, 1 590, 1 565, 1 535, 1 375, 1 355, 700, and 700 cm^{-1}; δ_H($CDCl_3$) 1.67 (1 H, t, *J* 9.3 Hz, SH), 1.87 (3 H, s, Me), 3.09 (1 H, A of ABX, *J* 9.3 Hz), 3.49 (1 H, B of ABX, *J* 9.3 Hz) (CH_2), 7.32 (1 H, s, =CH–), 7.33—7.60 (6 H, m, Ph), 8.09—8.35 (2 H, m, Ph), and 8.50—8.67 (2 H, m, Ph); δ_C($CDCl_3$) 25.5 (q, Me), 33.8 (t, CH_2), 48.1 (s, quaternary C), 121.1 (s, CN), 127.3 (d), 128.3 (d), 128.5 (d), 128.9 (d), 131.1 (d), 131.3 (d), 136.3 (s) 137.0 (s) (ArC), 111.8 (d), 164.5 (s), 165.4 (s), and 166.1 (s) (pyrimidine ring C).

Alkylthiopyrimidine (**6f**), b.p. 138 °C at 4 mmHg (Found: C, 70.05; H, 7.1; N, 10.65. $C_{15}H_{18}N_2S$ requires C, 69.7; H, 7.0; N, 10.85%); $\nu_{max.}$ 1 585, 1 560, 1 365, and 1 110 cm^{-1}; δ_H($CDCl_3$) 1.06 (6 H, d, *J* 6.4 Hz, Me), 1.89—2.17 (1 H, m, CH), 2.42 (3 H, s, Me), 3.18 (2 H, dd, *J* 14.2, 20.5 Hz, CH_2), 6.84 (1 H, s, =CH–), 7.36—7.49 (3 H, m, Ph), and 8.37—8.51 (2 H, m, Ph); δ_C($CDCl_3$) 22.0 (q, Me), 23.9 (q, Me), 28.6 (d, CH), 37.5 (t, CH_2), 128.2 (d), 130.1 (d), 137.7 (s) (ArC), 115.8 (d), 163.1 (s), 164.4 (s), and 169.6 (s) (pyrimidine ring C).

Mercaptoalkylated quinazoline (**9a**), b.p. 170 °C at 2 mmHg; m.p. 90.5—91.0 °C (Found: C, 59.35; H, 5.25; N, 10.5. $C_{13}H_{14}N_2O_2S$ requires C, 59.5; H, 5.35; N, 10.65%); $\nu_{max.}$(KBr) 2 560, 1 735, 1 615, 1 550, 1 495, 1 275, 1 205, 1 180, 1 110, 765, and 680 cm^{-1}; δ_H($CDCl_3$) 1.53 (1 H, t, *J* 8.8 Hz, SH), 1.86 (3 H, s, Me), 3.50 (2 H, d, *J* 8.8 Hz, CH_2), 3.67 (3 H, s, CO_2Me), 7.51—8.15 (4 H, m, ArH), and 9.29 (1 H, s, –N=CH–); δ_H($CDCl_3$) 22.8 (q, Me), 33.2 (t, CH_2), 52.6 (q, CO_2Me), 54.6 (s, quaternary C), 122.9 (s), 127.7 (d), 129.9 (d), 133.1 (d), 150.6 (s), 153.5 (d), 168.9 (s) (quinazoline ring C), and 174.6 (s, CO_2).

Mercaptoalkylated quinazoline (**9b**), m.p. 79.5—80 °C (Found: C, 63.1; H, 4.85; 18.2. $C_{12}H_{13}N_3S$ requires C, 62.85; H, 4.85; N, 18.3%); $\nu_{max.}$(KBr) 2 570, 2 240, 1 615, 1 560, 1 500, 780, and 675 cm^{-1}; δ_H($CDCl_3$) 2.01 (3 H, s, Me), 2.03 (1 H, X of ABX, *J* 8.3, 10.3 Hz, SH), 3.17 (1 H, A of ABX, *J* 10.3, 14.2 Hz), 3.75 (1 H, B of ABX, *J* 8.3, 14.2 Hz) (CH_2), 7.66—8.20 (3 H, m), 8.70 (1 H, dd, *J* 1.0, 7.8 Hz) (ArH), and 9.30 (1 H, –N=CH–); δ_C($CDCl_3$) 26.0 (q, Me), 33.5 (t, CH_2), 45.4 (s, quaternary C), 121.8 (s, CN), 122.3 (s), 124.2 (d), 128.2 (d), 130.1 (d), 134.0 (d), 151.2 (s), 153.4 (d), and 164.3 (s) (quinazoline ring C).

Mercaptoalkylated quinazoline (**9c**), b.p. 140 °C at 2 mmHg (Found: 60.55; H, 5.8; 10.35. $C_{14}H_{16}N_2O_2S$ requires C, 60.85; H, 5.85; N, 10.15%); $\nu_{max.}$(film) 2 575, 1 700, 1 615, 1 565, 1 495, 1 280, 1 235, 1 200, and 765 cm^{-1}; δ_H($CDCl_3$) 1.56 (1 H, t, *J* 8.8 Hz, SH), 1.83 (3 H, s, Me), 2.87 (3 H, s, Me), 3.48 (2 H, d, *J* 8.8 Hz, CH_2), 3.66 (3 H, s, CO_2Me), and 7.42—8.03 (4 H, m, ArH); δ_C($CDCl_3$) 22.8 (q, Me), 26.4 (q, Me), 33.3 (t, CH_2), 52.5 (q, CO_2Me), 54.4 (quatenary C), 120.7 (s), 123.8 (d), 126.6 (d), 129.2 (d), 132.9 (d), 151.1 (s), 162.7 (s), 168.7 (s) (quinazoline ring C), and 174.7 (s, CO_2).

Mercaptoalkylated quinazoline (**9d**), b.p. 145 °C at 2 mmHg (Found: C, 64.45; H, 5.45; N, 17.55. $C_{13}H_{13}N_3S$ requires C, 64.15; H, 5.4; N, 17.25%); $\nu_{max.}$(film) 2 580, 2 240, 1 615, 1 565, 1 495, and 770 cm^{-1}; δ_H($CDCl_3$) 2.02 (1 H, X of ABX, *J* 8.3, 19.3 Hz, SH), 1.98 (3 H, s, Me), 2.88 (3 H, s, Me), 3.14 (1 H, A of ABX, *J* 10.3, 14.2 Hz), 3.73 (1 H, B of ABX, *J* 8.3, 14.2 Hz) (CH_2), 7.55—8.09 (3 H, m), and 8.63 (1 H, br s) (ArH); δ_C($CDCl_3$) 26.0 (q, Me), 26.2 (q, Me), 33.4 (t), 45.3 (s, CH_2), 120.0 (s, CN), 121.8 (s), 124.1 (d), 127.1 (d), 129.3 (d), 133.8 (d), 151.6 (s), 162.7 (s), and 164.0 (s) (quinazoline ring C).

Mercaptoalkylated tetrahydroquinazoline (**10a**), m.p. 92—93.5 °C (Found: C, 66.35; H, 6.45; N, 8.1. $C_{19}H_{22}N_2O_2S$ requires C, 66.65; H, 6.45; N, 8.2%); $\nu_{max.}$(KBr) 2 575, 1 735, 1 535, 740, and 700 cm^{-1}; δ_H($CDCl_3$) 1.52 (1 H, t, *J* 8.8 Hz, SH), 1.64 (3 H, s, Me), 1.60—2.00 (4 H, m), 2.40—2.64 (2 H, m), 2.82—3.08 (2 H, m) (CH_2), 3.40 (2 H, d, *J* 8.8 Hz, CH_2), 3.70, (3 H, s,

CO_2Me), 7.35—7.45 (3 H, m, Ph), and 8.39—8.49 (2 H, m, Ph); $\delta_C(CDCl_3)$ 21.5 (q, Me), 22.1 (t), 22.4 (t), 25.0 (t), 32.9 (t), 33.2 (t) (CH_2), 52.3 (q, CO_2Me), 54.3 (s, quaternary C), 126.0 (s), 127.8 (d), 128.3 (d), 130.0 (d), 137.8 (s), 160.2 (s), 166.1 (s), 166.7 (s) (quinazoline ring C and Ph), and 174.2 (s, CO_2).

Mercaptoalkylated tetrahydroquinazoline (**10b**), m.p. 114—115 °C (Found: C, 69.8; H, 6.2; N, 13.65. $C_{18}H_{19}N_3S$ requires C, 69.85; H, 6.2; N, 13.6%); $\nu_{max.}$(KBr) 2 540, 2 240, 1 555, 1 545, 760, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 1.79 (3 H, s, Me), 1.75—2.05 (5 H, m, CH_2 and SH), 2.88—3.19 (5 H, m, CH_2 and A of ABX), 3.72 (1 H, B of ABX) (CH_2), 7.42—7.49 (3 H, m, Ph), and 8.31—8.48 (2 H, m, Ph); $\delta_C(CDCl_3)$ 21.8 (t), 22.4 (t), 25.7 (t), 33.2 (t), 33.7 (t) (CH_2), 25.0 (q, Me), 45.2 (s, quaternary C), 121.2 (s, CN), 126.8 (s), 127.8 (d), 128.5 (d), 130.5 (d), 137.3 (s), 160.7 (s), 161.0 (s), and 168.3 (s) (quinazoline ring C and Ph).

Mercaptoalkylated pyrimidine (**12a**), m.p. 97—99 °C (Found: C, 55.2; H, 6.85; N, 11.35. $C_{11}H_{16}N_2O_2S$ requires C, 54.9; H, 6.7; N, 11.65%) $\nu_{max.}$(KBr) 2 540, 1 735, 1 595, 1 230, and 1 105 cm^{-1}; $\delta_C(CDCl_3)$ 1.49 (1 H, t, *J* 9.3 Hz, SH), 1.69 (3 H, s, Me), 2.43 (6 H, s, Me), 3.26 (2 H, d, *J* 9.3 Hz, CH_2), 3.72 (3 H, s, CO_2Me), and 6.89 (1 H, s, =CH–); $\delta_H(CDCl_3)$ 21.5 (q, Me), 24.9 (q, Me), 32.5 (t, CH_2), 52.1 (q, CO_2Me), 56.8 (s, quaternary C), 118.1 (d), 166.5 (s), 169.7 (s) (pyrimidine ring C), and 174.1 (s, CO_2).

Mercaptoalkylated pyrimidine (**12b**), m.p. 81.5—82 °C (Found: C, 57.95; H, 6.35; N, 20.4. $C_{10}H_{13}N_3S$ requires C, 57.95; H, 6.3; N, 20.25%); $\nu_{max.}$(KBr) 2 560, 2 240, 1 595, 1 545, 1 340, and 1 275 cm^{-1}; $\delta_H(CDCl_3)$ 1.73 (1 H, X of ABX, *J* 9.3 Hz, SH), 1.81 (3 H, s, Me), 2.50 (6 H, s, Me), 3.07 (1 H, A of ABX, *J* 9.3, 13.7 Hz), 3.29 (1 H, B of ABX, *J* 9.3, 13.7 Hz) (CH_2), and 6.97 (1 H, s, =CH–); $\delta_C(CDCl_3)$ 23.9 (q, Me), 25.2 (q, Me), 33.7 (t, CH_2), 49.5 (s, quaternary C), 121.6 (s, CN), 118.9 (d), 166.0 (s), and 167.4 (s) (pyrimidine ring C).

Mercaptoalkylated pyrimidine (**12c**), b.p. 185 °C at 2 mmHg (Found: C, 69.45; H, 5.65; N, 7.54. $C_{21}H_{20}N_2O_2S$ requires C, 69.2; H, 5.55; N, 7.7%); $\nu_{max.}$(film) 2 580, 1 730, 1 590, 1 565, 1 535, 1 285, 1 235, 1 105, 755, and 695 cm^{-1}; $\delta_H(CDCl_3)$ 1.48 (1 H, t, *J* 8.8 Hz), 1.79 (3 H, s, Me), 3.35 (2 H, d, *J* 8.8 Hz, CH_2), 3.73 (3 H, s, CO_2Me), 7.31 (1 H, s, =CH–), 7.40—7.60 (6 H, m, Ph) 8.12—8.24 (2 H, m, Ph), and 8.55—8.66 (2 H, m, Ph); $\delta_C(CDCl_3)$ 21.3 (q, Me), 32.3 (t, CH_2), 52.4 (q, CO_2Me), 55.4 (s, quaternary C), 127.2 (d), 128.3 (d), 128.7 (d) 130.6 (d), 130.7 (d), 137.0 (s), 137.5 (s) (aromatic C), 111.7 (d), 163.7 (s), 164.4 (s), 169.9 (s) (pyrimidine ring C), and 173.6 (s, CO_2).

Mercaptoalkylated pyrimidine (**12d**), b.p. >250 °C at 2 mmHg (Found: C, 72.85; H, 5.15; N, 12.9. $C_{20}H_{17}N_3S$ requires C, 72.5; H, 5.15; N, 12.65%); $\nu_{max.}$(film) 2 560, 2 345, 1 590, 1 565, 1 535, 1 380, 780, 760, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 1.67 (1 H, X of ABX, *J* 9.3 Hz), 1.87 (3 H, s, Me), 3.09 (1 H, A of ABX, *J* 9.3, 13.7 Hz), 3.40 (1 H, B of ABX, *J* 9.3, 13.7 Hz), (CH_2), 7.32 (1 H, s, =CH–), 7.33—7.60 (6 H, m), 8.09—8.35 (2 H, m), and 8.50—8.67 (2 H, m) (ArH); $\delta_C(CDCl_3)$ 25.5 (q, Me), 33.8 (t, CH_2), 48.1 (s, quaternary C), 121.1 (s, CN), 127.3 (d), 128.3 (d), 128.5 (d), 128.9 (d), 131.1 (d), 131.3 (d), 136.3 (s), 137.0 (s) (ArC), 111.8 (d), 164.5 (s), 165.4 (s), and 166.1 (s) (pyrimidine ring C).

Mercaptoalkylated quinazoline (**14**), b.p. 200 °C at 2 mmHg (decomp.); $\nu_{max.}$(film) 2 560, 1 730, 1 605, 1 560, 1 540, 1 290, 1 195, 1 175, 770, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 1.57 (1 H, t, *J* 8.8 Hz, SH), 1.87 (3 H, s, Me), 3.46 (2 H, dd, *J* 1.0, 8.8 Hz, CH_2), 3.75 (3 H, s, CO_2Me), and 7.45—8.16 (9 H, m, Ph); $\delta_C(CDCl_3)$ 21.6 (q, Me), 32.5 (t, CH_2), 52.3 (q, CO_2Me), 57.2 (s, quaternary C), 121.4 (s), 126.8 (d), 127.3 (d), 128.4 (d), 128.9 (d), 129.9 (d), 130.2 (d), 133.4 (d), 137.1 (s), 151.2 (s), 165.8 (s), 168.0 (s) (ArC and quinazoline ring C), and 174.1 (s, CO_2). This compound (**14**) did not give the satisfactory microanalytical results since it decomposed during purification by distillation.

Mercaptoalkylated quinazolinone (**16a**), m.p. 144—145 °C (Found: C, 55.85; H, 5.1; N, 9.8. $C_{13}H_{14}N_2O_3S$ requires C, 56.1; H, 5.05; N, 10.05%); $\nu_{max.}$(KBr) 3 200, 3 140, 2 560, 1 745, 1 670, 1 615, 1 255, 1 200, 1 105, and 770 cm^{-1}; $\delta_H(CDCl_3)$ 1.59 (1 H, X of ABX, *J* 8.8 Hz, SH), 1.87 (3 H, s, Me), 3.25 (1 H, A of ABX, *J* 8.8, 13.7 Hz), 3.47 (1 H, B of ABX, *J* 8.8, 13.7 Hz) (CH_2), 3.77 (3 H, s, CO_2Me), 7.25—7.56 (2 H, m), 7.81—8.07 (2 H, m) (quinazoline ring H); $\delta_C(CDCl_3)$ 23.0 (q, Me), 33.4 (t, CH_2), 52.9 (q, CO_2Me), 54.4 (s, quaternary C), 121.5 (d), 123.3 (d), 125.3 (d), 126.1 (d), 135.2 (s), 152.6 (s) (quinazoline ring C), 171.5 (s, CO), and 172.5 (s, CO_2).

Mercaptoalkylated quinazolinone (**16b**), m.p. 153—155 °C (Found: C, 58.55; H, 4.5; N, 16.9. $C_{12}H_{11}N_3OS$ requires C, 58.75; H, 4.5; N, 17.15%); $\nu_{max.}$(KBr) 3 190, 3 130, 2 240, 1 660, 1 605, and 765 cm^{-1}; $\delta_H(CDCl_3)$ 1.97 (1 H, t, *J* 9.3 Hz, SH), 2.02 (3 H, s, Me), 3.13—3.67 (2 H, m, CH_2), 7.48—7.70 (1 H, m), 7.75—7.95 (2 H, m), and 8.32 (1 H, t of d, *J* 1.0, 7.3 Hz) (quinazoline ring H); $\delta_C(CDCl_3)$ 23.7 (q, Me), 32.6 (t, CH_2), 47.5 (s, quaternary C), 119.4 (s, CN), 120.8 (s), 126.5 (d), 127.9 (d), 128.2 (d), 135.4 (d), 148.1 (d), 151.3 (s) (quinazoline ring C), and 163.9 (s, CO).

Mercaptoalkylated benzimidazo[1,2-*c*]quinazoline (**18**), m.p. 145—146 °C (Found: C, 65.05; H, 4.95; N, 11.7. $C_{19}H_{17}N_3O_2S$ requires C, 64.95; H, 4.85; N, 11.95%); $\nu_{max.}$(KBr) 2 560, 1 735, 1 625, 1 595, 1 535, 1 275, 1 240, 1 225, 760, and 740 cm^{-1}; $\delta_H(CDCl_3)$ 2.07 (3 H, s, Me), 2.08—2.28 (1 H, m, SH), 3.18—3.42 (1 H, m), 3.80 (1 H, B of ABX, *J* 6.8, 7.3 Hz) (CH_2), 7.31—8.09 (7 H, m), and 8.63—8.78 (1 H, m) (ArH); $\delta_H(CDCl_3)$ 21.8 (q, Me), 34.8 (t, CH_2), 52.8 (q, CO_2Me), 55.7 (s, quaternary C), 114.5 (d), 118.6 (s), 120.5 (d), 123.0 (d), 124.2 (d), 125.3 (d), 127.9 (d), 128.5 (s), 131.6 (d), 140.7 (s), 144.1 (s), 148.1 (s), 148.7 (s) (ring C), and 173.4 (s, CO_2).

Thermal Reaction of Pyrimidine-4(3H)-*thione* (**1a**) *with Styrene* (**4e**).—A solution of pyrimidine-4(3*H*)-thione (**1a**) (202 mg) and styrene (312 mg) in benzene (80 ml) was refluxed for 2 days. The mixture was cooled, the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column with benzene–hexane (4:1) as eluant to give the alkylthiopyrimidine (**6e′**) (66%), b.p. 150 °C at 4 mmHg (Found: C, 74.45; H, 5.85; N, 9.05. $C_{19}H_{18}N_2S$ requires C, 74.45; H, 5.9; N, 9.15%); $\nu_{max.}$($CHCl_3$) 1 560 and 1 360 cm^{-1}; $\delta_H(CDCl_3)$ 1.80 (3 H, d, *J* 7.3 Hz, Me), 2.37 (3 H, s, Me), 5.35 (1 H, q, *J* 7.3 Hz, CH), 6.76 (1 H, s, =CH–), 7.21—7.51 (8 H, m, Ph), and 8.39—8.50 (2 H, m, Ph); $\delta_C(CDCl_3)$ 22.4 (q), 23.8 (q, Me), 42.6 (d, CH), 127.2 (d), 128.2 (d), 128.5 (d), 130.4 (d), 137.7 (s), 142.7 (s) (ArC), 115.7 (d), 163.2 (s), 164.7 (s), and 168.9 (s) (pyrimidine ring C).

Sensitization and Quenching of Pyrimidine-4(3H)-*thione* (**1a**) *with compound* (**4c**).—(*a*) *Sensitization.* A solution of pyrimidine-4(3*H*)-thione (**1a**) (200 mg), methyl methacrylate (**4a**) (*ca.* 1 ml), and Michler's ketone (E_T = 62 kcal mol^{-1}, in such a ratio that the sensitizer absorbs the incident light more than 95%) in benzene (80 ml) was irradiated at 366 nm light under argon for 8 h. Work-up gave the mercaptoalkylated pyrimidine (**5a**) in low yield (5%) and more than 95% of starting pyrimidinethione (**1a**) was recovered

(*b*) *Quenching.* A solution of (**1a**) (200 mg), (**4a**) (*ca.* 1 ml), and cyclo-octatetraene (260 mg, 2.5 equiv. molar) in benzene (80 ml) was irradiated under the same conditions. Work-up gave the mercaptoalkylated pyrimidine (**5a**) in 48% yield. Penta-1,3-diene (E_T = 59.2 kcal mol^{-1}) as a triplet quencher reacted with pyrimidinethione (**1a**) to give a mixture of 1:1-adducts of (**1a**) and neither penta-1,3-diene nor the mercaptoalkylated pyrimidine (**5a**) were detected.

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