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Reaction of Heterocyclic Ketene Aminals with Aryl Isothiocyanates and Synthesis of Sulfur Containing Heterocycles Therefrom

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ABSTRACT

Heterocyclic ketene aminals reacted with aryl isothiocyanates to give products of addition to the β-carbon. By oxidative cyclization of these addition products by the action of bromine, isothiazole-fused heterocycles or benzothiazole-substituted heterocyclic ketene aminals were formed according to the influence of the different substituents.

INTRODUCTION

Heterocyclic ketene aminals are versatile starting materials for the synthesis of a wide variety of fused heterocycles. Thus, the synthesis and reactions of heterocyclic ketene aminals have attracted much attention recently. Due to the effect of conjugation of the two electron-donating amino groups on the double bond, the β-carbon of heterocyclic ketene aminals possesses a significantly high electron density. Therefore, they may function as nucleophiles, with the reactions taking place always at the β-carbon. Examples of such reactions are nucleophilic addition to α, β-unsaturated esters [1–6], azodicarboxylate [3], aryl azides [7–9], or benzonitrile oxides [10,11] and nucleophilic substitution with benzyl chloride or bromoacetate [12]. However, the reaction of heterocyclic ketene aminals with isothiocyanates has been studied only in a few cases [13–15]. Here, we wish to report the results of the reactions of heterocyclic ketene aminals **1** and **2** with aryl isothiocyanates and the syntheses of sulfur-containing heterocycles therefrom.

RESULTS AND DISCUSSION

Heterocyclic ketene aminals **1** and **2** were prepared from ketene mercaptals and the corresponding diamines. The reaction of nitromethane or benzophenones with sodium hydride and carbon disulfide, followed by treatment with methyl iodide, served well to synthesize the ketene mercaptals. The two types of reaction could be carried out in a one-pot reaction [16,17]. Compound **1** or **2** reacted smoothly with phenyl or 4-fluorophenyl isothiocyanate in acetonitrile solution to give a yellow-greenish solid product in good to excellent yield. The reaction conditions, yields, melting points, and elemental analyses are listed in Table 1.

It has been reported in the literature [13] that the nitroketene aminals **1a** and **2a** did not react with phenyl isothiocyanate and only reacted with more reactive isothiocyanates such as benzoyl isothiocyanate [14] or ethoxycarbonyl isothiocyanate [15]. However, in our hands, these two nitroketene aminals reacted with phenyl isothiocyanate to give the addition products in 50% and 64% yields, re-

Dedicated to Professor Yao-Zeng Huang on the occasion of his eightieth birthday.

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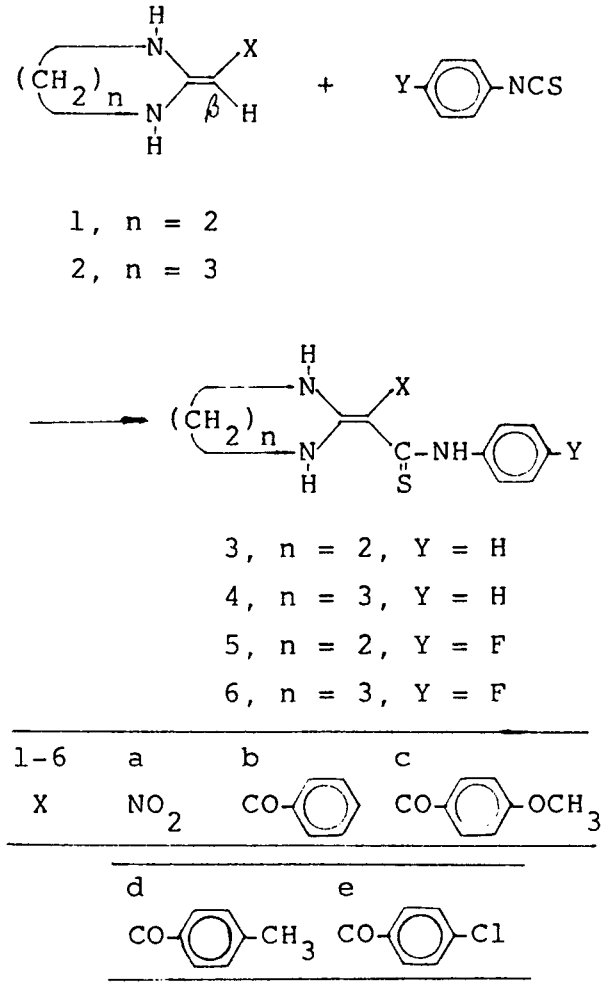


Formula 1

spectively. Consequently, selection of an optimal preparative procedure for this reaction was thought to be necessary. Under ideal conditions, the reactions of benzoyl-substituted heterocyclic ketene aminals with aryl isothiocyanates proceeded successfully and always gave excellent yields of products.

The constitutions of the reaction products were confirmed by elemental analyses and by mass spectra to be 1:1 molar ratio addition products. The absence of an ethylenic proton signal in the ^{1}H-NMR spectra excludes the *N*-addition product **A**, and the absence of a methine proton signal in the ^{1}H-NMR spectra and the presence of a ketone carbonyl carbon signal in the ^{13}C-NMR spectra of benzoyl substituted compounds also exclude the amidine form **B** or enol-amidine form **C**. Therefore, the structures of the products were deemed to be β-carbon addition product **3–6**, and other spectroscopic data were also consistent with these structures.

The addition products **3** and **4** can be oxidatively cyclized by reaction with bromine, followed by alkali workup to give the final product in low to moderate yield. The 4-fluorophenyl compounds **5** and **6** reacted less readily with bromine than the compounds **3** and **4**. The yields, melting points, and elemental analyses are listed in Table 2.

From the mass spectral data, the molecular peaks of all the products are found to be two less than those of the starting materials. However, in the ^{1}H-NMR spectra, a deuterium exchangeable signal corresponding to one proton is present in the spectrum of each of **7a** and **8a**, while there are two such protons in the spectra of the other benzoyl substituted compounds. It is therefore indicated that there are two kinds of structures for the products. The structures of fused isothiazole heterocycles for **7a** and **8a** are further confirmed by the complicated pattern of the CH_2 units linked to nitrogen atoms in the 1,3-diazaheterocyclic ring. The presence of 10 aromatic carbon signals in the ^{13}C-NMR spectra of benzoyl substituted compounds indicates that these compounds are benzothiazole ring substituted heterocyclic ketene aminals. The two structures for the products produced by the oxidative cyclization with bromine of the adducts of nitroketene aminals with isothiocyanate have been reported once in the literature [15], but the circumstances of their preparation were quite different from those reported here.

In conclusion, heterocyclic ketene aminals can react with aryl isothiocyanates to afford β-carbon addition products. This indicates that the nucleophilicity of the β-carbon in heterocyclic ketene aminals is stronger than that of the nitrogen atoms. According to the different substituents, isothiazole fused heterocycles or benzothiazole ring substituted heterocyclic ketene aminals are formed by the oxidative cyclization of the adducts by the action of bromine.

EXPERIMENTAL

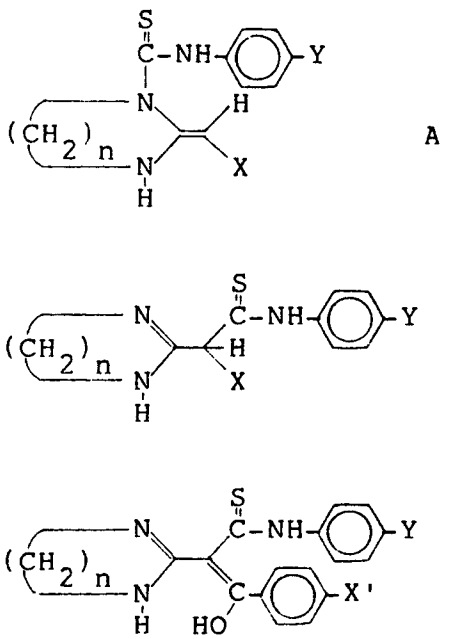
Melting points are uncorrected. The NMR spectra were measured with Varian EM-360 ML, Jeol-90Q, and Jeol-FX-100 spectrometers. IR spectra were recorded on a Perkin-Elmer 684 spectrometer using KBr pellets. UV spectra were recorded on a Hitachi 340 spectrometer in ethanol solution. Mass spectra were determined at 25 eV for **3–6** and at 70 eV for **7–10** on a AEI MS-50 spectrometer. Elemental analyses were carried out by the Analytical Laboratory of the Institute of Chemistry and Nankai University.

General Procedure for the Reaction of **1** *and* **2** *with Aryl Isothiocyanates*

A mixture of **1** or **2** (2 mmol) and aryl isothiocyanate (2.5 mmol) in 1 5 mL of dried acetonitrile was refluxed for 5–15 minutes, and then stirred at room temperature for 1–3 days (as shown in Table 1).

TABLE 1 The Reaction Conditions, Yield, Melting Point, and Elemental Analysis of Compounds **3–6**

Compound	Reaction Conditions: Reflux, Min	Reaction Conditions: RT, Day	Yield (%)	MP (°C)	Found, % (Calculated): C	H	N
3a		3	50	164–165	49.96(49.98)	4.61(4.58)	21.13(21.20)
3b	15	3	90	162–163.5	67.06(66.85)	5.29(5.30)	13.20(12.99)
3c	15	1	91	161–163	64.49(64.57)	5.50(5.42)	11.80(11.89)
3d	15	2	82	249–250	67.66(67.63)	5.67(5.68)	12.58(12.45)
3e	15	1	95	246–247.5	60.31(60.41)	4.58(4.51)	11.71(11.74)
4a	10	2	64	159–160	51.59(51.78)	5.02(5.07)	19.96(20.13)
4b	5	1	97	204–205.5	67.70(67.63)	5.82(5.68)	12.81(12.45)
4c	5	1	100	211–212	65.26(65.37)	5.80(5.76)	11.64(11.44)
4d	5	1	100	232–234	68.37(68.34)	5.95(6.02)	11.90(11.96)
4e	5	1	100	202–203	61.15(61.36)	4.86(4.88)	11.24(11.30)
5b	5	1	97	128–129	63.61(63.32)	4.74(4.72)	12.28(12.30)
5c	5	1	97	159–160.5	61.26(61.44)	4.88(4.88)	11.33(11.31)
5d	15	1	100	248–249	64.12(64.20)	5.11(5.10)	12.17(11.82)
5e	15	1	94	249–250.5	57.49(57.52)	4.03(4.02)	10.92(11.18)
6b	15	1	83	193–196	64.29(64.20)	4.75(5.10)	12.00(11.82)
6c	15	1	100	214–215.5	61.62(62.32)	5.34(5.23)	10.83(10.90)
6d	15	1	81	240–242	65.21(65.02)	5.49(5.46)	11.81(11.37)
6e	15	1	65	220–221	58.89(58.53)	4.04(4.40)	11.04(10.78)



Formula 2

The crude product was filtered off, and then purified by washing with hot ethyl acetate or by column chromatography (ethyl acetate/ethanol).

2-[(Nitro)(phenylthiocarbamoyl)methylene] imidazolidine

3a: MS: m/z 265 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 345 (4.25), 282 (4.33), 223 nm (4.45). IR: 3310, 3200 (NH), 1545, 1378 (NO_2), 1130 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 12.67 (1H, s), 9.08 (2H, s), 6.85–7.95 (5H, m), 3.78 (4H, s).

2-[(Benzoyl)(phenylthiocarbamoyl)methylene] imidazolidine

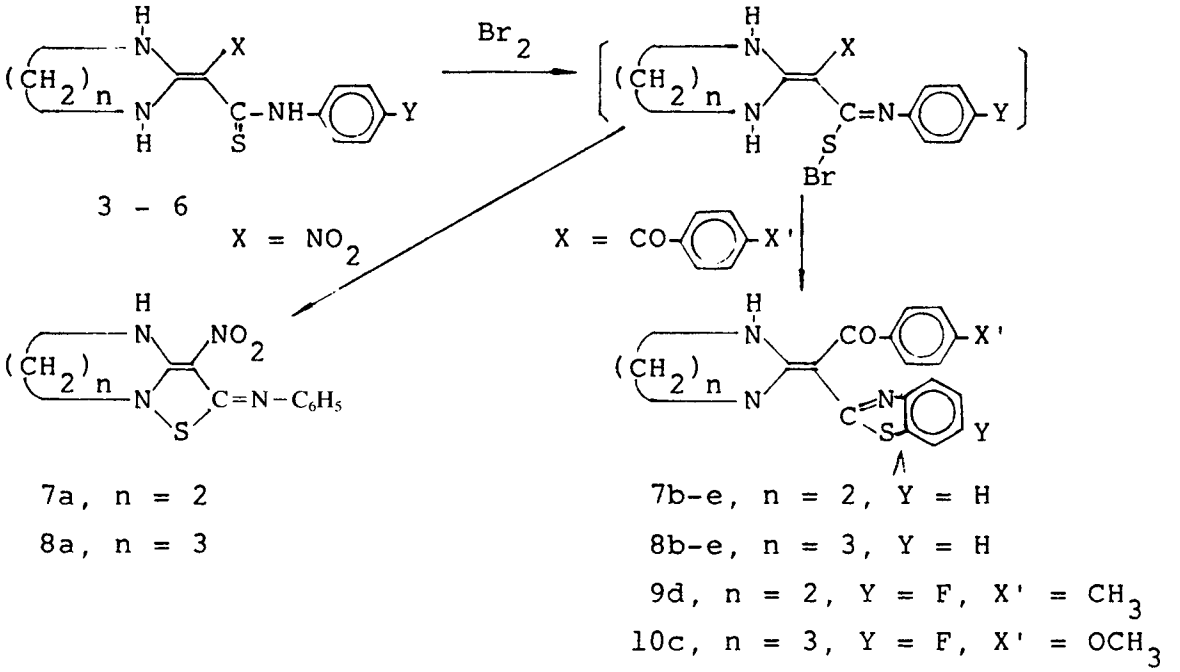
3b: MS: m/z 323 (M^+). UV: λ_{max} (1g ϵ) 316 (4.20), 233 (4.06), 209 nm (4.07). IR: 3260, 3120 (NH), 1585 (C=O), 1565, 1525, 1120 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 11.15 (1H, s), 9.12 (2H, s), 7.18–7.48 (10H, m), 3.71 (4H, s).

2-[(4-Methoxybenzoyl)(phenylthiocarbamoyl) methylene] imidazolidine

3c: MS: m/z 354 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 310 (4.14), 215 nm (4.05). IR: 3270, 3150 (NH), 1595 (C=O), 1580, 1515, 1120 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 11.07 (1H, s), 9.02 (2H, s), 7.43 (2H, d), 6.77 (2H, d), 7.12–7.28 (5H, m), 3.71 (3H, s), 3.62 (4H, s).

2-[(4-Methylbenzoyl)(phenylthiocarbamoyl) methylene] imidazolidine

3d: MS: m/z 338 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 313 (4.28), 238 (sh), 210 nm (4.28). IR: 3245, 3200 (NH), 1575 (C=O), 1558, 1525, 1118 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 11.70 (1H, s), 9.11 (2H, s), 7.46 (2H, d), 6.90 (2H, d), 7.16–7.26 (5H, m), 3.65 (4H, s), 2.35 (3H, s). ^{13}C-NMR ($CDCl_3$): δ 194.2, 189.7, 166.5, 140.6, 139.0, 138.8, 128.8, 128.3, 127.9, 125.7, 123.8, 99.1, 43.2, 21.3.



7,8	b	c	d	e
X'	H	OCH_3	CH_3	Cl

Formula 3

2-[(4-Chlorobenzoyl)(phenylthiocarbamoyl) methylene] imidazolidine

3e: MS: *m/z* 358 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 320 (4.54), 236 (4.54), 208 nm (4.68). IR: 3260, 3160 (NH), 1585 (C=O), 1560, 1525, 1120 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 11.29 (1H, s), 9.15 (2H, s), 7.75 (2H, d), 7.29 (2H, d), 7.16–7.26 (5H, m), 3.55 (4H, s). ^{13}C-NMR ($CDCl_3$): δ 194.7, 188.0, 166.3, 139.9, 138.8, 136.2, 129.3, 128.7, 128.1, 125.8, 123.3, 99.2, 43.3.

2-[(Nitro)(phenylthiocarbamoyl)methylene] hexahydropyrimidine

4a: MS: *m/z* 279 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 360 (4.30), 222 (4.32), 209 nm (4.34). IR: 3230, 3140 (NH), 1540, 1350 (NO_2), 1150 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 13.52 (1H, s), 9.60 (2H, s), 7.12–7.84 (5H, m), 3.44 (4H, t), 2.00 (2H, quin).

2-[(Benzoyl)(phenylthiocarbamoyl)methylene] hexahydropyrimidine

4b: MS: *m/z* 337 (M^+). UV: λ_{max} (1g ϵ) 329 (4.06), 284 (4.02), 224 (4.43), 210 nm (4.31). IR: 3240, 3180 (NH), 1610 (C=O), 1590, 1560, 1055 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 14.44 (1H, s), 9.24 (2H, s), 7.04–7.84 (10H, m), 3.12 (4H, t), 1.60 (2H, quin).

2-[(4-Methoxybenzoyl)(phenylthiocarbamoyl) methylene] hexahydropyrimidine

4c: MS: *m/z* 367 (M^+). UV: λ_{max} (1g ϵ) 328 (4.49), 260 (4.55), 208 nm (4.68). IR: 3240, 3190 (NH), 1610 (C=O), 1595, 1565, 1058 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 14.48 (1H, s), 9.24 (2H, s), 7.74 (2H, d), 6.82 (2H, d), 7.02–7.44 (5H, m), 3.76 (3H, s), 3.16 (4H, t), 1.68 (2H, quin).

2-[(4-Methylbenzoyl)(phenylthiocarbamoyl) methylene] hexahydropyrimidine

4d: MS: *m/z* 352 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 327 (3.90), 282 (4.12), 226 (4.43), 208 nm (4.52). IR: 3240, 3190 (NH), 1610 (C=O), 1590, 1560, 1055 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 14.19 (1H, s), 9.25 (2H, s), 7.68 (2H, d), 7.04 (2H, d), 7.16–7.36 (5H, m), 3.18 (4H, t), 2.32 (3H, s), 1.72 (2H, quin). ^{13}C-NMR δ ($CDCl_3$): 187.5, 181.4, 161.7, 139.6, 139.3, 136.9, 126.9, 126.8, 125.6, 123.0, 122.4, 104.2, 37.6, 20.1, 17.0.

2-[(4-Chlorobenzoyl)(phenylthiocarbamoyl) methylene] hexahydropyrimidine

4e: MS: *m/z* 372 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 336 (5.05), 219 (4.97), 209 nm (5.00). IR: 3235, 3180 (NH), 1610

TABLE 2 The Yield, Melting Point, and Elemental Analysis of Compounds **7–10**

Compound	Yield (%)	MP, °C (Solvent)	Found, % (Calculated)		
			C	H	N
7a	15	173–174.5 (CH_2Cl_2/C_6H_{12})	50.08(50.37)	3.89(3.84)	20.87(21.36)
7b	20	226–227 (CH_3OH)	66.84(67.27)	5.14(4.70)	12.94(13.07)
7c	37	245–246.5 (CH_3OH)	65.04(64.93)	4.78(4.88)	11.68(11.96)
7d	29	241–242 (CH_3OH)	67.94(68.03)	5.10(5.11)	12.95(12.53)
7e	42	267–268.5 (CH_2Cl_2/C_6H_{12})	60.84(60.75)	4.03(3.97)	12.07(11.81)
8a	7	189–191 (CH_2Cl_2/C_6H_{12})	51.64(52.16)	4.16(4.38)	19.95(20.28)
8b	53	182–184 (CH_3OH)	67.73(68.03)	5.03(5.11)	12.63(12.53)
8c	49	117–118 (CH_3OH)	65.33(65.73)	5.24(5.24)	11.17(11.50)
8d	34	154–155 (CH_3OH)	68.80(68.74)	5.49(5.48)	11.93(12.03)
8e	38	161–162.5 (CH_2Cl_2/C_6H_{12})	61.54(61.70)	4.35(4.36)	11.44(11.36)
9d	7.5	238–240 (CH_3OH)	64.66(64.57)	4.44(4.56)	11.68(11.89)
10c	34	121–123 (CH_3OH)	62.40(62.65)	5.26(4.73)	10.94(10.96)

(C=O), 1590, 1560, 1050 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 12.99 (1H, s), 9.50 (2H, s), 7.48 (2H, d), 7.16 (2H, d), 7.19–7.44 (5H, m), 3.27 (4H, t), 1.83 (2H, quin). ^{13}C-NMR ($CDCl_3$): δ 187.8, 179.6, 161.4, 140.6, 139.5, 132.6, 127.2, 127.0, 126.5, 123.3, 122.3, 104.2, 37.7, 17.0.

2-[(Benzoyl)(4-fluorophenylthiocarbamoyl)methylene] imidazolidine

5b: MS: *m/z* 342 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 322 (4.21), 225 (4.10), 207 nm (4.13). IR: 3225, 3175 (NH), 1590 (C=O), 1570, 1502, 1120 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 11.12 (1H, s), 9.13 (2H, s), 6.85–7.52 (9H, m), 3.67 (4H, s).

2-[(4-Methoxybenzoyl)(4-fluorophenylthiocarbamoyl)methylene] imidazolidine

5c: MS: *m/z* 372 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 322 (4.21), 217 nm (4.61). IR: 3260, 3180 (NH), 1585 (C=O), 1565, 1530, 1500, 1120 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 11.25 (1H, s), 9.05 (2H, s), 7.46 (2H, d), 6.79 (2H, d), 6.97–7.11 (4H, m), 3.73 (3H, s), 3.65 (4H, s).

2-[(4-Methylbenzoyl)(4-fluorophenylthiocarbamoyl)methylene] imidazolidine

5d: MS: *m/z* 356 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 320 (4.01), 242 (4.11), 212 nm (4.15). IR: 3240, 3120 (NH), 1585 (C=O), 1565, 1520, 1500, 1118 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 11.10 (1H, s), 9.10 (2H, s), 7.45 (2H, d), 6.93 (2H, d), 7.14–7.26 (4H, m), 3.67 (4H, s), 2.32 (3H, s).

2-[(4-Chlorobenzoyl)(4-fluorophenylthiocarbamoyl)methylene] imidazolidine

5e: MS: *m/z* 376 $(M + 1)^+$. UV: λ_{max} (1g ϵ) 324 (4.15), 244 (4.20), 207 nm (4.10). IR: 3250, 3180 (NH), 1580 (C=O), 1530, 1500, 1130 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 11.13 (1H, s), 9.05(2H, s), 7.72 (2H, d), 7.09 (2H, d) 7.23–7.47 (4H, m), 3.68 (4H, s).

2-[(Benzoyl)(4-fluorophenylthiocarbamoyl)methylene] hexahydropyrimidine

6b: MS: *m/z* 355 (M^+). UV: λ_{max} (1g ϵ) 335 (4.65), 221 (4.60), 208 nm (4.61). IR: 3220, 3180 (NH), 1615 (C=O), 1505, 1050 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 14.40 (1H, s), 9.24 (2H, s). 6.96–7.80 (9H, m), 3.12 (4H, t), 1.60 (2H, quin).

2-[(4-Methoxybenzoyl)(4-fluorophenylthiocarbamoyl)methylene] hexahydropyrimidine

6c: MS: *m/z* 385 (M^+). UV: λ_{max} (1g ϵ) 327 (4.10), 258 (4.33), 212 nm (4.48). IR: 3220, 3180 (NH), 1615 (C=O), 1600, 1495, 1058 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 14.00 (1H, s), 9.28 (2H, s), 7.74 (2H, d), 6.82 (2H, d), 7.03–7.46 (4H, m), 3.76 (3H, s), 3.20 (4H, t), 1.75 (2H, quin).

2-[(4-Methylbenzoyl)(4-fluorophenylthiocarbamoyl)methylene] hexahydropyrimidine

6d: MS: *m/z* 369 (M^+). UV: λ_{max} (1g ϵ) 336 (3.78), 220 (3.99), 208 nm (4.05). IR: 3225, 3180 (NH), 1615 (C=O), 1505, 1055 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 14.48 (1H, s), 9.20 (2H, s), 7.70 (2H, d), 6.98 (2H, d), 7.12–7.36 (4H, m), 3.12 (4H, t), 2.32 (3H, s), 1.65 (2H, quin).

2-[(4-Chlorobenzoyl)(4-fluorophenylthiocarbamoyl)methylene] hexahydropyrimidine

6e: MS: *m/z* 389 (M^+). UV: λ_{max} (1g ϵ) 337 (4.84), 221 (4.70), 208 nm (4.75). IR: 3180, 3125 (NH), 1620 (C=O), 1575, 1500, 1055 cm^{-1} (C=S). ^{1}H-NMR (DMSO-d_6): δ 13.12 (1H, s), 9.44 (2H, s), 7.42 (2H, d), 6.90 (2H, d), 7.02–7.44 (4H, m), 3.28 (4h, t), 1.76 (2H, quin).

General Procedure for the Oxidative Cyclization of **3–6** *to* **7–10** *by the Action of Bromine*

A solution of bromine (1.2 mmol) in 5 mL of chloroform was added dropwise to a solution of **3–6** (1 mmol) in 20 mL of chloroform at room temperature during 45 minutes. Twenty milliliters of water were added to the reaction mixture to dissolve the yellowish solid that had formed, and the mixture was neutralized with saturated sodium bicarbonate solution. The organic layer was separated, and the water layer was extracted with chloroform (3 × 20 mL). The organic solution was combined, washed, and dried with anhydrous sodium sulfate. After removal of solvent, the crude product was crystallized from methanol or a mixture of methylene chloride and cyclohexane. In the case of **7a** and **8a**, methylene chloride was used as the solvent.

2-Phenylimino-3-nitro-5,6-dihydro-2H-4H-imidazo[1,2-b]isothiazole

7a: MS: *m/z* 262 (M^+). UV: λ_{max} (1g ϵ) 358 (3.66), 305 (3.74), 238 nm (4.00). IR: 3270 (NH), 1575, 1350 (NO_2), 1607 cm^{-1}. ^{1}H-NMR (DMSO-d_6): δ 9.30 (1H, s), 6.85–7.40 (5H, m), 3.90, 3.70 (4H, A_2B_2).

2-[Benzoyl-2-(imidazolidinylidene)]methyl-benzothiazole

7b: MS: *m/z* 321 (M^+). UV: λ_{max} (1g ϵ) 317 (4.96), 240 (5.06), 210 nm (5.03). IR: 3275 (NH), 1590 (C=O), 1545 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.80 (2H, s), 7.04–7.76 (9H, m), 3.84 (4H, s).

2-[(4-Methoxybenzoyl)-2-(imidazolidinylidene)]methyl-benzothiazole

7c: MS: *m/z* 351 (M^+). UV: λ_{max} (1g ϵ) 320 (3.44), 255 (3.40), 225 nm (3.43). IR: 3240 (NH), 1580 (C=O), 1540 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.68 (2H, s), 7.74 (2H, d), 6.85 (2H, d), 7.12–7.52 (4H, m), 3.88 (3H, s), 3.84 (4H, s).

2-[(4-Methylbenzoyl)-2-(imidazolidinylidene)]methyl-benzothiazole

7d: MS: *m/z* 335 (M^+). UV: λ_{max} (1g ϵ) 319 (4.29), 241 (4.32), 210 nm (4.22). IR: 3280 (NH), 1580 (C=O), 1537 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.76 (2H, s), 7.72 (2H, d), 7.16 (2H, d), 7.20–7.56 (4H, m), 3.84 (4H, s), 2.40 (3H, s). ^{13}C-NMR ($CDCl_3$): δ 191.8, 169.8, 165.2, 151.4, 140.2, 139.2, 133.7, 129.0, 128.7, 125.3, 122.9, 120.4, 120.0, 91.2, 43.4, 21.5.

2-[(4-Chlorobenzoyl)-2-(imidazolidinylidene)]methyl-benzothiazole

7e: MS: *m/z* 355 (M^+). UV: λ_{max} (1g ϵ) 317 (4.28), 240 (4.39), 214 nm (4.32). ^{1}H-NMR ($CDCl_3$): δ 9.76 (2H, s), 7.76 (2H, d), 7.12 (2H, d), 7.28–7.60 (4H, m), 3.90 (4H, s). ^{13}C-NMR ($CDCl_3$): δ 187.9, 167.8, 163.9, 150.4, 139.8, 134.3, 132.4, 129.0, 127.3, 124.2, 121.8, 119.2, 119.1, 89.6, 42.3.

2-Phenylimino-3-nitro-4,5,6,7-tetrahydro-2H-isothiazolo[2,3-a]pyrimidine

8a: MS: *m/z* 276 (M^+). UV: λ_{max} (1g ϵ) 355 (3.90), 313 (3.97), 233 (4.30), 215 nm (4.24). IR: 3290 (NH), 1577, 1370 (NO_2), 1615 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.04 (1H, s), 6.90–7.36 (5H, m), 3.50 (2H, t), 3.42 (2H, t), 2.14 (2H, quin).

2-[Benzoyl-2-(hexahydropyrimidinylidene)]methyl-benzothiazole

8b: MS: *m/z* 335 (M^+). UV: λ_{max} (1g ϵ) 343 (4.05), 307 (4.08), 222 (4.40), 208 nm (4.34). IR: 3240 (NH), 1620 (C=O), 1593, 1530 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 11.16 (2H, s), 7.04–7.76 (9H, m), 3.50 (4H, t), 2.02 (2H, quin).

2-[(4-Methoxybenzoyl)-2-(hexahydropyrimidinylidene)]methyl-benzothiazole

8c: MS: *m/z* 365 (M^+). UV: λ_{max} (1g ϵ) 350 (4.12), 305 (4.15), 259 (4.27), 220 nm (4.41). IR: 3145 (NH), 1620 (C=O), 1575, 1507 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 11.08 (2H, s), 7.75 (2H, d), 6.83 (2H, d), 7.12–7.52 (4H, m), 3.84 (3H, s), 3.52 (4H, t), 2.04 (2H, quin).

2-[(4-Methylbenzoyl)-2-(hexahydropyrimidinylidene)]methyl-benzothiazole

8d: MS: *m/z* 349 (M^+). UV: λ_{max} (1g ϵ) 347 (4.09), 309 (4.10), 222 (4.37), 212 nm (4.34). IR: 3200 (NH), 1600 (C=O), 1530 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 11.16 (2H, s), 7.72 (2H, d), 7.10 (2H, d), 7.16–7.52 (4H, m), 3.52 (4H, t), 2.40 (3H, s), 2.00 (2H, quin).

2-[(4-Chlorobenzoyl)-2-(hexahydropyrimidinylidene)]methyl-benzothiazole

8e: MS: *m/z* 369 (M^+). UV: λ_{max} (1g ϵ) 350 (4.02), 314 (4.03), 224 nm (4.39). IR: 3200 (NH), 1595

(C=O), 1532 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 10.96 (2H, s), 7.74 (2H, d), 7.18 (2H, d), 7.28–7.55 (4H, m), 3.50 (4H, t), 2.02 (2H, quin). ^{13}C-NMR ($CDCl_3$): δ 189.0, 170.4, 158.2, 150.8, 141.1, 135.6, 133.8, 130.5, 128.4, 125.3, 123.2, 120.3, 120.2, 91.8, 38.3, 19.6.

2-[(4-Methylbenzoyl)-2-(imidazolidinylidene)]methyl-6-fluorobenzothiazole

9d: MS: *m/z* 353 (M^+). UV: λ_{max} (1g ϵ) 322 (3.73), 243 (3.77), 213 nm (3.73). IR: 3290 (NH), 1583 (C=O), 1540 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 9.68 (2H, s), 7.64 (2H, d), 6.96 (2H, d), 7.04–7.56 (3H, m), 3.88 (4H, s), 2.40 (3H, s).

2-[(4-Methoxybenzoyl)-2-(hexahydropyrimidinylidene)]methyl-6-fluorobenzothiazole

10c: MS: *m/z* 383 (M^+). UV: λ_{max} (1g ϵ) 349 (4.13), 304 (4.16), 255 (4.38), 218 nm (4.43). IR: 3180 (NH), 1620 (C=O), 1600 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 11.12 (2H, s), 7.70 (2H, d), 6.82 (2H, d), 7.04–7.52 (3H, m), 3.84 (3H, s), 3.50 (4H, t), 2.00 (2H, quin).

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