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Hetero-*Diels-Alder* Reaction of some 1,3-Diaza-1,3-butadienes with Ketenes. Synthesis of Functionalized Pyrimido[1,2-*b*]-benzothiazoles and 1,3,4-Thiadiazolo-[3,2-*a*]pyrimidines

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Summary. Reaction of 1,3-diaza-1,3-butadienes (**1a–c**) with various ketenes and chloroketenes results in the formation of substituted 4-oxo-pyrimido[2,1-*b*]benzothiazoles (**4a–d**) and 1,3,4-thiadiazolo[3,2-*a*]pyrimido-4-ones (**4e,f**). Reaction of 1,3-diaza-1,3-butadienes **1d,e** with ketenes and chloroketenes leads to the 2-morpholine-substituted compounds **7** and **15**, respectively. All reactions proceed *via* formation of [4 + 2] cycloadducts that eliminate methylthiol, methylsulfenyl chloride, or morpholine.

Keywords. Hetero *Diels-Alder* Reaction; 1,3-Diaza-1,3-butadienes; Ketenes; Pyrimido[1,2-*b*]benzothiazoles; 1,3,4-Thiadiazolo[3,2-*a*]pyrimidines.

Hetero-*Diels-Alder*-Reaktion einiger 1,3-Diaza-1,3-butadiene mit Ketenen. Synthese funktionalisierter Pyrimido[1,2-*b*]benzothiazole und 1,3,4-Thiadiazolo[3,2-*a*]pyrimidine

Zusammenfassung. Die Reaktion der 1,3-Diaza-1,3-butadiene **1a–c** mit verschiedenen Ketenen und Chlorketenen führt zu substituierten 4-Oxo-pyrimido[2,1-*b*]benzothiazolen (**4a–d**) und 1,3,4-Thiadiazolo[3,2-*a*]pyrimido-4-onen (**4e, f**). Die 1,3-Diaza-1,3-butadiene **1d,e** ergeben mit Ketenen und Chlorketenen die 2-Morpholin-substituierten Verbindungen **7** und **15**. Alle Reaktionen verlaufen über [4 + 2]-Cycloaddukte, die Methylthiol, Methylsulfenylchlorid oder Morpholin eliminieren.

Introduction

The hetero-*Diels-Alder* reaction is one of the most effective tools for the construction of a wide variety of six-membered heterocycles with a broad substitution pattern [1]. Among these reactions, dienes containing one or two nitrogen atoms have attracted considerable attention because of their importance in natural products synthesis [2, 3]. Numerous examples of [4 + 2] cycloadditions of simple conjugated azadienes and their 1,2 or 1,4-diaza analogues have been published. In each case these dienes were substituted with strong electron donating groups capable of enhancing their reactivity towards typical electron-deficient dienophiles [4, 5]. In contrast, conjugated 1,3-diazadienes have been rarely used for *Diels-Alder* reactions due to the

difficulties encountered in their preparation and their low reactivity in heterodiene cycloadditions.

Continuing our study on the reactivity of azometines and enamines [6, 7], we now present the result of reactions of some conjugated 1,3-diazadienes with ketenes. Cycloaddition of ketenes to the C=N double bond of imines leads to the formation of [2+2] cycloadducts (β-lactams). On the other hand, the reaction of ketenes with compounds bearing a conjugated C=N double bond affords [4+2] and/or [2+2] cycloadducts [8, 9]. The type of cycloaddition depends on the position of the nitrogen atoms in the dienic system, as well as on the substituents in the ketenes. For example, cycloaddition of various ketenes to 1,4-diaza-1,3-butadienes derived from glyoxal leads to the formation of β-lactams and *bis*-β-lactams [10]. Similarly, the reaction of dimethyl- and diphenylketene with 1,4-diaza-1,3- butadienes derived from benzil or diacetyl gives β-lactams [10], whereas the cycloaddition of 1,3-diaza-1,3-butadienes to diphenylketene yields [4+2] cycloadducts [11].

Results and Discussion

In this paper, we present investigations on the cycloaddition of various ketenes and chloroketenes to dialkyl N-(2-benzothiazolyl)- (**1a,b**) and dimethyl-N-(1,3,4-thiadiazolyl)-dithiocarbonimidates (**1c**) serving as 1,3-diaza-1,3-butadienes. The synthesis of the dienes **1a,b** was accomplished by reaction of 2-aminothiazole with carbon disulfide and methyl or ethyl iodide in dimethylformamide in the presence of sodium hydroxide [12]. Diene **1c** was prepared in the same way from 2-amino-1,3,4-thiadiazole. In dienes **1**, one of the imine moieties is stabilized by the heteroaromatic ring, whereas the second is activated by strong electron donating substituents.

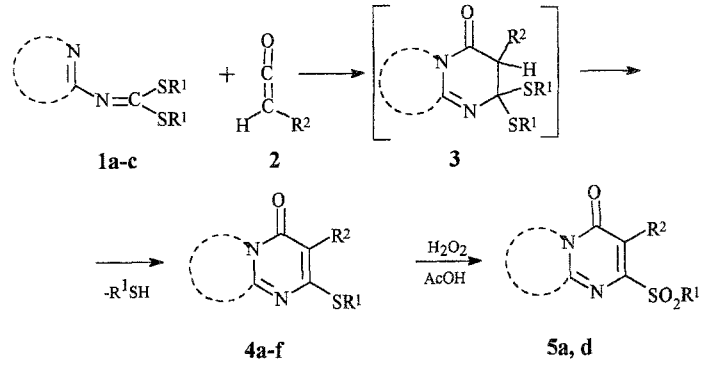
The reaction of 1,3-diazadienes **1a–c** with ketenes **2**, generated *in situ* from the appropriate acetyl chloride and an excess of triethylamine in methylene chloride solution, resulted in compounds **4** (Scheme 1) in moderate to good yields (65–77%). The structure of the products was established on the basis of analytical and spectroscopic data.

For example, the IR spectrum of **4a** reveals a band at 1659 cm^{-1} indicating the presence of an α,β-unsaturated carbonyl group. Its ^1H NMR spectrum shows a singlet of one methyl group at $\delta = 2.45$ ppm and a multiplet at $\delta = 7.34$–8.89 ppm of nine aromatic protons.

Molecular weight determination by mass spectroscopy ($m/z = 324$) indicated that the reaction of **1** to **2** is followed by elimination of methylthiol. The key step of this reaction is the [4+2] cycloaddition resulting in an intermediate **3** that undergoes base assisted elimination of methylthiol yielding **4**. The formation of compounds **4** is outlined in Scheme 1.

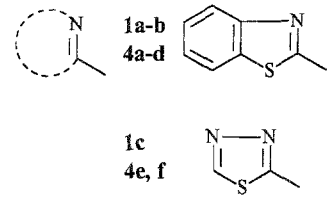
The presence of an alkylthio function in compounds **4** prompted us to study their behaviour with respect to oxidizing and nucleophilic agents. When **4a** was reacted with hydrogen peroxide in a solution of acetic acid, the alkylthio group was oxidized to a sulfone yielding **5** (Scheme 1). However, all attempts to replace the alkylthio group in **4** by hydroxy or by amine (*e.g.* morpholine) were unsuccessful.

Since the direct introduction of an amine function in **4a** failed, we examined an alternative procedure involving cycloaddition. It was found that diene **1a** reacts readily with morpholine in boiling ethanolic solution in a molar ratio of 1:1 and 1:2 furnishing dienes **1d** and **1e**, respectively (Scheme 2).

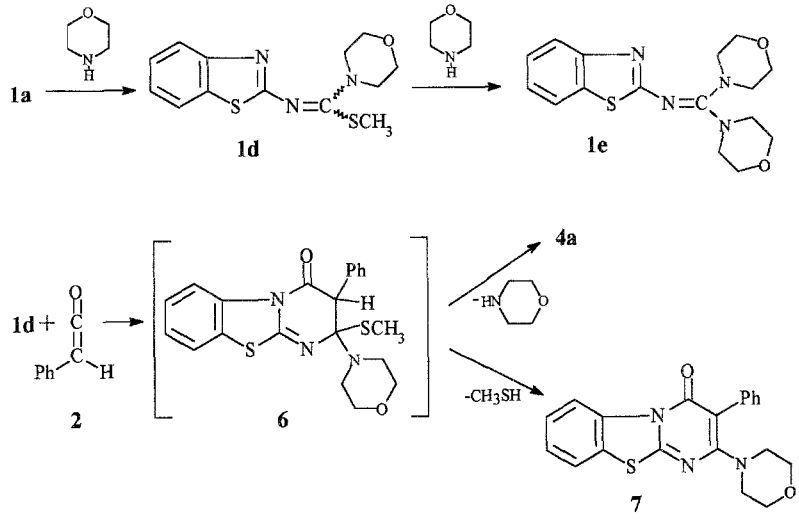


1	R^1
a	CH_3
b	C_2H_5
c	CH_3

4, 5	R^1	R^2
a	CH_3	Ph
b	CH_3	OPh
c	CH_3	PhtN
d	C_2H_5	Ph
e	CH_3	Ph
f	CH_3	OPh



Scheme 1



Scheme 2

Reaction of the 1,3-diazadiene **1d**, containing methylthio and morpholine substituents, with phenylketene (**2**) afforded a mixture of compounds **4a** and **7** (Scheme 2). Their presence was detected by gas chromatography, and their ratio in the crude reaction mixture was determined by ^{1}H NMR spectroscopy (**4a**: **7** = 1:1.1).

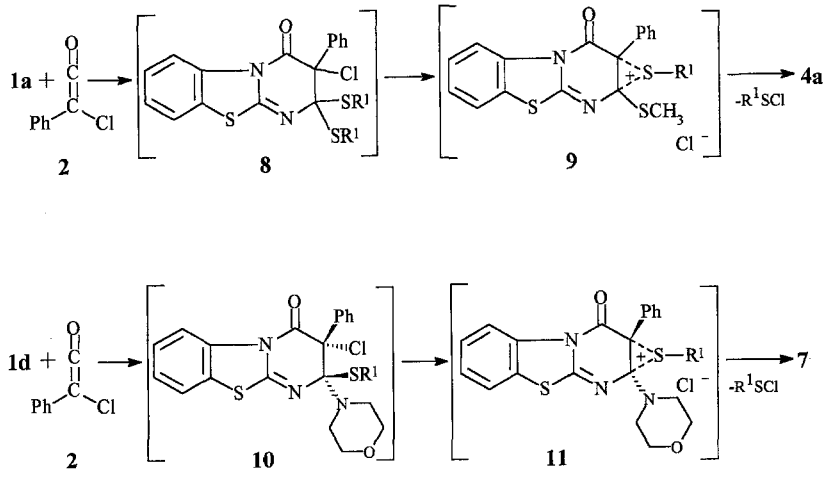
The ^{1}H NMR spectrum of **7** reveals multiplets of eight protons at $\delta = 3.17$ and 4.45 ppm (morpholine moiety), but does not show the signal of a methylthio group. Aromatic protons resonate at $\delta = 7.27$–8.82 ppm. Analytical data combined with molecular mass determination ($m/z = 363$) confirm the structure of **7**.

The formation of both compounds **4a** and **7** indicates that the reaction of **1d** and phenylketene (**2**) leads to a [4+2] cycloadduct (**6**) as a mixture of two diastereoisomers. Elimination of morpholine from **6** yields compound **4a**, whereas elimination of methylthiol gives **7** (Scheme 2).

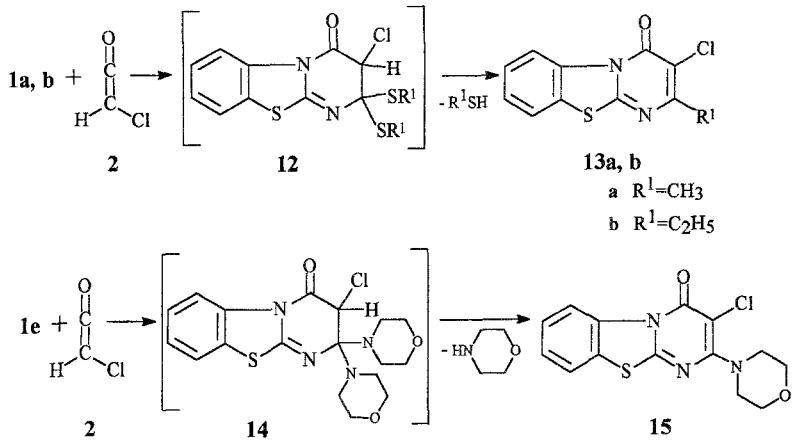
We then extended the cycloaddition of **1** to chloroketenes generated from appropriate chloroacetic chlorides. The reaction of **1a** with chlorophenylketene (**2**) carried out under similar conditions as above afforded compound **4a** in excellent yield (80%). Thus, in this case the cycloaddition of **1a** to **2** is followed by the elimination of methylsulfenyl chloride. The most likely pathway involving the transformation of the primary cycloadduct **8** into product **4a** proceeds *via* an episulfonium intermediate (**9**, [13, 14]). It is formed by nucleophilic attack of the sulfur of the methylthio group on the neighbouring carbon atom C-3 bearing a chlorine substituent. The episulfonium intermediate **9** eliminates methylsulfenyl chloride furnishing **4a** (Scheme 3).

A similar mechanism operates in the reaction of chlorophenylketene (**2**) with diene **1d** bearing methylthio and morpholine substituents, resulting in compound **7** as the sole product. The exclusive formation of **7** may be explained as follows: Owing to sterical reasons, the cycloaddition of chlorophenylketene to diene **1d** leads to the intermediate cycloadduct **10** having the favoured stereochemistry for nucleophilic attack of sulfur of the methylthio group on the carbon atom C-3 a bearing chlorine substituent. Elimination of methylsulfenyl chloride from episulfonium intermediate **11** furnishes compound **7** (Scheme 3).

The above results and the efficiency of these reactions prompted us to investigate the cycloadditions of dienes **1** to chloroketene **2**. The reaction of **1a** with chloroketene, generated from chloroacetic chloride in the presence of triethylamine, yields compounds **13a** (Scheme 4) in very good yield (80%). Its analytical and spectroscopic data combined with a molecular mass of 282 indicated the presence of a chlorine substituent. Thus, in this case the cycloaddition of **1a** and chloroketene is followed by elimination of methylthiol. Similar results were obtained by reaction of



Scheme 3



Scheme 4

diene **1b** with chloroketene yielding **13b** (Scheme 4). However, the reaction of diene **1e** with chloroketene yielding compound **15** (Scheme 4). However, the reaction of diene **1e** with chloroketene yielding compound **15** is accompanied by elimination of morpholine from the intermediate cycloadduct **14** (Scheme 4).

The above reactions allow us to present some general remarks and conclusions:

i) The cycloaddition of 1,3-diaza-1,3-butadienes **1** to ketenes presents an efficient method for the synthesis of pyrimidones fused with a heterocyclic system.

ii) Reactions of dienes **1** with ketenes or chloroketenes proceed *via* formation of [4+2] cycloadducts and are followed by elimination of methylthiol or methylsulfenyl chloride or amine, respectively.

iii) Elimination of methylthiol from the intermediate cycloadducts occur easier than elimination of methylsulfenyl chloride or amine.

Experimental

Melting points were determined on a Boetius hot stage apparatus. IR spectra: Bruker IFS 48, KBr pellets. ^{1}H and ^{13}C NMR spectra: Bruker AMX 500 (500.14 MHz for ^{1}H and 125.77 MHz for ^{13}C) in $CDCl_3$ and *DMSO*-d_6 with *TMS* as an internal standard. MS: Finningan Mat 95 (70 eV). Microanalyses: Perkin Elmer Analyser 240.

1,3-Diaza-1,3-butadienes (**1a–c**)

Dienes **1a** and **1b** were obtained according to procedures describe in Ref. [12]. Compound **1c** (not yet described) was obtained in a similar way.

Dimethyl N-(2-thiadiazolyl)-dithiocarbonimidate (**1c**)

Pale yellow crystals from methanol Yield: 40%; m.p.: 50 °C; IR (KBr, ν (cm^{-1})): 1660 (C=N); ^{1}H NMR ($CDCl_3$): $\delta = 2.61$ (s, 6H, SCH_3), 8.93 (s, 1H, CH) ppm.

1-Methylthio-1-morpholine-methyleneamine-(2-benzothiazole) (**1d**)

To an ethanolic solution (50 ml) of **1a** (1.0 g), 0.35 ml of morpholine in 10 ml of ethanol were added. The reaction mixture was refluxed for 3 h. The solvent was partly evaporated and the residue was collected by filtration.

Pale yellow crystals from methanol. Yield: 65%; m.p.: 82–85 °C; IR (KBr, ν (cm^{-1})): 1588 (C=N); ^{1}H NMR ($CDCl_3$): $\delta = 1.31$ (s, 3H, SCH_3), 4.17 (s, 8H, CH_2) 7.03–7.98 (m, 5H, CH) ppm.

1,1-Dimorpholine-metylenoamine-(2-benzothiazole) (**1e**)

Compound **1e** was obtained in the same way as **1d** by treating diene **1a** with a twofold excess of morpholine and refluxing the ethanolic solution for 5 h. The solvent was evaporated. The residue was treated with methanol. The precipitate was filtered off and purified by crystallization from methanol.

Pale yellow crystals from methanol. Yield: 50%; m.p.: 120–122 °C; IR (KBr, ν(cm^{-1})): 1592 (C=N); ^{1}H NMR ($CDCl_3$): $\delta = 3.32$–3.71 (s, 16H, CH_2), 7.14–7.66 (m, 4H, CH arom) ppm.

Reaction of diene **1a**–**e** *with ketenes and chloroketenes; general procedure*

To a stirred and cooled (0–5 °C) solution of diene **1a** (10 mmol) and triethylamine (15 mmol) in 50 ml of dry methylene chloride, the appropriate acid chloride dissolved in methylene chloride (20 ml) was added dropwise. The reaction mixture was stirred for 1 h. and subsequently refluxed for 2 h. After standing overnight, the precipitate was filtered off and washed with water and ethanol. The crude products were purified by crystallization from acetonitrile.

4a: Colourless prisms (65%); m.p.: 257–260 °C; IR (KBr, ν(cm^{-1})): 1659 (CO); ^{1}H NMR (*DMSO*-d_6): $\delta = 2.45$ (s, 3H, SCH_3), 7.37 (m, 3H, CH arom.), 7.45 (m, 2H, CH arom.), 7.57 (m, 2H, CH arom.), 8.08 (m, 1H, CH arom.), 8.89 (m, 1H, CH arom.) ppm; ^{13}C NMR (*DMSO*-d_6): $\delta = 13.44$ (SCH_3), 115.39, 118.83, 123.05, 123.96, 126.92, 126.97, 127.94, 128.26, 130.57, 133.04 (C arom.), 135.99, (C-3), 157.77 (C-2), 160.16 (C-10a), 162.17 (C-4) ppm; MS (m/z(%)): 324(100) M^+, 309(38) $[C_{16}H_9N_2OS_2]^+$, 277(6) $[C_{16}H_9N_2OS]^+$, 263(16), 249(24) $[C_{15}H_9N_2S]^+$, 162(4) $[C_8H_4NSO]^+$, 134(2%) $[C_7H_4NS]^+$, 89(18) $[C_7H_5]^+$, 77 $[C_6H_5]^+$; $C_{17}H_{12}N_2OS_2$ (324.42); calcd.: C 62.94, H 3.73, N 8.64, S 19.76; found: C 63.03, H 3.68, N 8.60, S 19.43.

4b: Colourless prisms (70%, 34%); m.p.: 252–255 °C; IR (KBr, ν(cm^{-1})): 1672 (CO); ^{1}H NMR (*DMSO*-d_6): $\delta = 2.53$ (s, 3H, SCH_3), 7.05 (d, 3H, CH arom.), 7.32 (m, 2H, CH arom.), 7.61 (m, 2H CH arom.), 8.12 (m, 1H, CH arom.), 8.89 (m, 1H, CH arom.) ppm; MS (m/z(%)): 340(100) M^+, 325(5) $[C_{16}H_9N_2O_2S_2]^+$, 293(2) $[C_{16}H_9N_2O_2S]^+$, 263(5) $[C_{11}H_7N_2O_2S_2]^+$, 235(5) $[C_{10}H_7N_2OS_2]^+$, 207(45) $[C_8H_4N_2S_2]^+$, 92(30) $[C_{10}H_8O_2S]^+$, 134(6) $[C_7H_4NS]^+$, 105(24) $[C_6H_5CO]^+$, 77(10) $[C_6H_5]^+$; $C_{17}H_{12}N_2O_2S_2$ (340.42); calcd.: C 59.98, H 3.55, N 8.23, S 18.84; found: C 60.15, H 3.55, N 8.24, S 18.96.

4c: Colourless prisms (70%); m.p.: 380 °C; IR (KBr, ν(cm^{-1})): 1672 (CO), 1726 (CO), 1785 (CO); ^{1}H NMR (*DMSO*-d_6): $\delta = 2.55$ (s, 3H, SCH_3), 7.62 (m, 2H, CH arom.), 7.99 (m, 2H, CH arom.), 8.05 (m, 2H, CH arom.), 8.14 (m, 1H, CH arom.), 8.81 (m, 1H, CH arom.) ppm; MS (m/z(%)): 393 M^+ (100), 346(3) $[C_{18}H_8N_3O_3S]^+$, 332(30) $[C_{18}H_8N_2O_3S]^+$, 246(13) $[C_{11}H_6N_2OS_2]^+$, 218(34) $[C_{10}H_6N_2S_2]^+$, 158(40) $[C_7H_4N_2S]^+$, 134(13) $[C_7H_4NS]^+$, 77(28) $[C_6H_5]^+$; $C_{19}H_{11}N_3O_3S_2$ (393.44); calcd.: N 10.68; found: N 10.66.

4d: Colourless prisms (44%); m.p.: 235–237 °C; IR (KBr, $\nu(cm^{-1})$): 1651 (CO); ^1H NMR (*DMSO*-d_6): $\delta = 1.24$ (t, 3H, CH_3), 3.08 (q, 2H, SCH_2), 7.33–7.46 (m, 5H, CH arom.), 7.56 (m, 2H, CH arom.), 8.07 (m, 1H, CH arom.), 8.88 (m, 1H, CH arom.) ppm; MS (*m/z* (%)): 338 (100) M^+, 323 (6) $[C_{17}H_{11}N_2OS_2]^+$, 309 (43) $[C_{16}H_9N_2OS_2]^+$, 277 (25) $[C_{16}H_9N_2OS]^+$, 249 (40) $[C_{15}H_9N_2S]^+$, 177 (30) $[C_8H_5N_2OS]^+$, 146 (9), 134 (6%) $[C_7H_4NS]^+$, 89 (21) $[C_7H_5]^+$; $C_{18}H_{14}N_2OS_2$ (338.44); calcd.: C 63.88, H 4.17, N 8.28, S 18.95; found: C 63.22, H 4.11, N 8.32, S 18.94.

7-Methylthio-5-oxo-6-phenyl-5H-1,3,4-thiadiazole[3,2-a]pyrimidine (**4e**)

Colourless prisms (30%); m.p.: 255–257 °C; IR (KBr, $\nu(cm^{-1})$): 1668 (CO); ^1H NMR (*DMSO*-d_6): $\delta = 2.42$ (s, 3H, SCH_3), 7.30–7.45 (m, 5H, CH arom.), 9.34 (s, 1H, CH) ppm; MS (*m/z* (%)): 275 (94) M^+, 260 (100) $[C_{11}H_6N_3OS_2]$, 228 (13) $[C_{11}H_6N_3OS]^+$, 200 (13) $[C_{10}H_6N_3S]^+$, 128 (10) $[C_3H_2N_3OS]^+$, 89 (9) $[C_7H_5]^+$, 85 (16) $[C_6H_5N]^+$, 77 (3) $[C_6H_5]^+$; $C_{12}H_9N_3OS_2$ (275.34); calcd.: C 52.35, H 3.30, N 15.26, S 23.29; found: C 52.09, H 3.10, N 15.49, S 23.50.

7-Methylthio-5-oxo-6-phenoxy-5H-1,3,4-thiadiazole[3,2-a]pyrimidine (**4f**)

Colourless prisms (28%); m.p.: 250–252 °C; IR (KBr, $\nu(cm^{-1})$): 1672 (CO); ^1H NMR (*DMSO*-d_6): $\delta = 2.45$ (s, 3H, SCH_3), 6.96–7.30 (m, 5H, CH arom.), 9.36 (s, 1H, CH) ppm; MS (*m/z* (%)): 291 (100%) M^+, 276 (7) $[C_{11}H_6N_3O_2S_2]^+$, 244 (2) $[C_{11}H_6N_3O_2S]^+$, 220 (2) $[C_{10}H_8N_2O_2S]^+$, 158 (17) $[C_9H_6N_2O]^+$, 105 (12) $[C_7H_5O]^+$, 77 (8) $[C_6H_5]^+$; $C_{12}H_9N_3O_2S_2$ (291.34); calcd.: C 49.47, H 3.11, N 14.42, S 22.01; found: C 48.83, H 2.72, N 14.35, S 21.90.

2-Morpholine-4-oxo-3-phenyl-4H-pyrimido[2,1-b]benzothiazole (**7**)

Colourless prisms (52%); m.p.: 190–193 °C; IR (KBr, $\nu(cm^{-1})$): 1651 (CO); ^1H NMR (*DMSO*-d_6): $\delta = 3.17$ (t, 4H, CH_2), 3.45 (t, 4H, CH_2), 7.27 (m, 1H, CH arom.), 7.40 (m, 4H, CH arom.), 7.48 (m, 2H, CH arom.), 7.98 (m, 1H, CH arom.), 8.82 (m, 1H, CH arom.) ppm; MS (*m/z* (%)): 363 M^+ (100), 304 (23) $[C_{19}H_{18}N_3O]^+$, 277 (8) $[C_{16}H_9N_2OS]^+$, 249 (26) $[C_{15}H_9N_2S]^+$, 134 (6) $[C_7H_4NS]^+$, 89 (13) $[C_7H_5]^+$, 77 (3) $[C_6H_5]^+$; $C_{20}H_{17}N_3O_2S$ (363.43); calcd.: C 66.10, H 4.71, N 11.56, S 8.82; found: C 65.57, H 4.41, N 11.63, S 9.03.

3-Chloro-2-methylthio-4-oxo-4H-pyrimido[2,1-b]benzothiazole (**13a**)

Colourless prisms (77%); m.p.: 224–226 °C; IR (KBr, $\nu(cm^{-1})$): 1680 (CO); ^1H NMR (*DMSO*-d_6): $\delta = 2.57$ (s, 3H, SCH_3), 7.60 (m, 2H, CH arom.), 8.08 (m, 1H, CH arom.), 8.88 (m, 1H, CH arom.) ppm; MS (*m/z* (%)): 282 M^+ (100), 247 (59) $[C_{10}H_4ClN_2OS_2]^+$, 235 (12) $[C_{10}H_4ClN_2OS]^+$, 219 (65) $[C_{10}H_7N_2S_2]^+$, 207 (47) $[C_9H_7N_2S_2]^+$, 192 (9) $[C_5H_3ClNOS_2]^+$, 134 (29) $[C_7H_4NS]^+$, 77 (41) $[C_6H_5]^+$; $C_{11}H_7ClN_2OS_2$ (282.76); calcd.: C 46.73, H 2.50, N 9.91, S 22.68; found: C 46.46, H 2.57, N 9.93, S 22.94.

3-Chloro-2-ethylthio-4-oxo-4H-pyrimido[2,1-b]benzothiazole (**13b**)

Colourless prisms (42%); m.p.: 178–180 °C; IR (KBr, νcm^{-1}): 1674 (CO); ^1H NMR (*DMSO*-d_6): $\delta = 1.31$ (m, 3H, CH_3), 3.17 (m, 2H, SCH_2), 7.59 (m, 2H, CH arom.), 8.04 (m, 1H, CH arom.), 8.86 (m, 1H, CH arom.) ppm; MS (*m/z* (%)): 296 M^+ (100), 281 (23) $[C_{11}H_6ClN_2OS_2]^+$, 268 (21) $[C_{11}H_9ClN_2S_2]^+$, 261 (86) $[C_{12}H_9N_2OS_2]^+$, 233 (20) $[C_{11}H_9N_2S_2]^+$, 207 (20) $[C_9H_4ClN_2S]^+$, 177 (23) $[C_8H_5SN_2O]^+$, 108 (3) $[C_6H_4S]^+$, 90 (3) $[C_6H_4N]^+$; $C_{12}H_9ClN_2OS_2$ (296.79); calcd.: C48.56, H 3.06, N 9.44, S 21.60; found: C 48.35, H 2.97, N 9.49, S 21.60.

3-Chloro-2-morpholine-4-oxo-4H-pyrimido[2,1-b]benzothiazole (**15**)

Colourless prisms (48%); m.p.: 188–190 °C; IR (KBr, $\nu(cm^{-1})$): 1668 (CO); ^1H NMR (*DMSO*-d_6): $\delta = 3.77$ (t, 4H, CH_2), 3.82 (m, 4H, CH_2), 7.44 (m, 1H, CH arom.), 7.51 (m, 1H, CH arom.), 7.63 (m, 1H, CH arom.), 9.03 (m, 1H, CH arom.) ppm; MS (*m/z*(%)): 321 (100) M^+, 286 (43) $[C_{14}H_{12}N_3O_2S]^+$, 264 (31) $[C_{11}H_7ClN_3OS]^+$, 236 (20) $[C_{10}H_5ClN_2OS]^+$, 208 (27) $[C_9H_5ClN_2S]^+$, 201 (25) $[C_{10}H_5N_2OS]^+$, 173 (7) $[C_9H_5N_2S]^+$; $C_{14}H_{12}ClN_3O_2S$ (321.78); calcd.: C 52.26, H 3.76, N 13.06, S 9.96; found: C 52.37, H 3.68, N 12.74, S 10.20.

(4-oxo-3-phenyl-4H-pyrimido[2,1,-b]benzothiazole)-2-methylsulfone (**5a**)

To a stirred and cooled (0–5 °C) solution of compound **4a** (10 mmol) in 150 ml glacial acetic acid, a solution of hydrogen peroxide (10 ml, 30%) was added dropwise. The reaction mixture was stirred for 48 h at room temperature and subsequently heated for 4 h at 60 °C. After cooling, the excess of hydrogen peroxide was decomposed by addition of oxalic acid. The solution was partly evaporated; the precipitate was filtered off, washed with water and recrystallized from acetonitrile. Sulfone **5d** was synthesized in a similar way.

5a: Colourless prisms (60%); m.p.: 285–287 °C; IR (KBr, $\nu(cm^{-1})$): 1680 (CO), 1320, 1143 (SO_2); ^1H NMR (*DMSO*-d_6): $\delta = 3.23$ (s, 3H, CH_3), 7.36–7.42 (m, 5H, CH arom.), 7.64 (m, 2H, CH arom.), 8.17 (m, 1H, CH arom.), 8.89 (m, 1H, CH arom.) ppm; MS (*m/z*(%)): 356 M^+ (100), 293 (33) $[C_{16}H_9N_2O_2S]^+$, 277 (53) $[C_{16}H_9N_2OS]^+$, 249 (81) $[C_{15}H_9N_2S]^+$, 237 (42) $[C_{14}H_9N_2S]^+$, 177 (7) $[C_{10}H_5N_2OS]^+$, 89 (23) $[C_7H_5]^+$, 63 (7) $[CH_3SO]^+$; $C_{17}H_{12}N_2O_3S_2$ (356.41); calcd.: C 57.29, H 3.39, N 7.86, S 17.99; found: C 57.54, H 3.47, N 7.77, S 17.45.

5d: Colourless prisms (54%); m.p.: 274–276 °C; IR (KBr, $\nu(cm^{-1})$): 1680 (CO), 1320, 1130 (SO_2); ^1H NMR (*DMSO*-d_6): $\delta = 1.17$ (t, 3H, CH_3), 3.38 (q, 2H, SCH_2), 7.34–7.43 (m, 5H, CH arom.), 7.63 (m, 2H, CH arom.), 8.16 (m, 1H, CH arom.), 8.88 (m, 1H, CH arom.) ppm; MS (*m/z*(%)): 372 M^+ (20), 370 (100), 294 (37) $[C_{16}H_9N_2O_2S]^+$, 277 (67) $[C_{16}H_9N_2OS]^+$, 249 (65) $[C_{15}H_9N_2S]^+$, 237 (22) $[C_{14}H_9N_2S]^+$, 89 (18) $[C_7H_5]^+$, 63 (3) $[CH_3SO]^+$; $C_{18}H_{14}N_2O_3S_2$ (370.44); calcd.: C 7.56, S 17.31; found: N 7.77, S 17.58.

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