Reaction of *N,N'*-Dialkyldithiodianilines with β-Ketoesters. A New Synthesis of *N*-Alkyl-2-acyl-3-oxo-3,4-dihydro-1,4-benzothiazines

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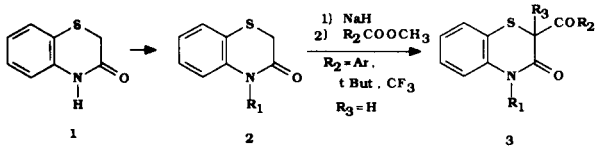
Received December 8, 1991

The title compounds **3a-j** together with the *N*-alkylacylketene *S,N*-acetals **12a-j** were obtained by reaction of *N,N'*-dialkyldithiodianilines with β-ketoesters compounds. A possible reaction pathway is suggested.

J. Heterocyclic Chem., **29**, 1155 (1992).

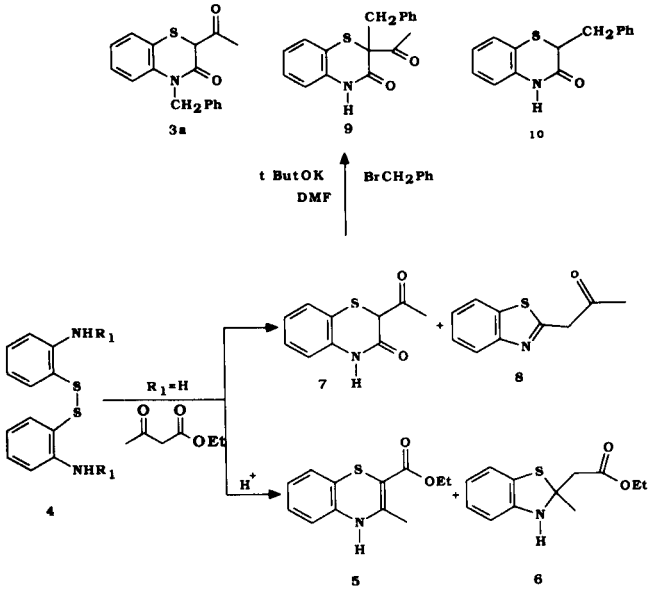
A Squibb patent [1] described the synthesis and antiinflammatory properties of some *N*-alkyl-2-acyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazines **3** (Scheme 1). These compounds were prepared by deprotonation of the *N*-alkylbenzothiazinone **2** with sodium hydride and successive reaction with carboxylic esters lacking α-hydrogen.

Scheme 1



As part of our research program aimed at exploring the potential biological activities of *N*-alkyl-2-acyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine compounds it was necessary to establish a general and more convenient synthesis. At this purpose the synthesis of the model compound **3a** (Scheme 2) was preliminarly attempted by treating the known [2] 2-acetyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine **7** at first with potassium *tert*-butoxide and then with benzyl bromide (BzBr) according to the procedure [3] used for *N*-alkylating the 3-oxo-3,4-dihydro-2H-1,4-benzothiazine **1**.

Scheme 2



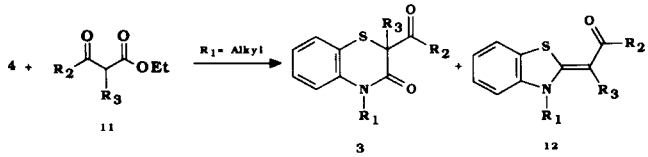
However, by using **7**, potassium *tert*-butoxide and BzBr in equimolar ratios, the benzothiazine **9** in high yield (85%) instead of the desired isomer **3a** was obtained. Moreover, by doubling the amount of *tert*-butoxide in the reaction the compounds **3a**, **9** and **10**, in 20%, 5% and 45% yield, respectively, were obtained. The products **3a**, **9** and **10** were characterized by their ir and ^{1}H-nmr spectra (see Experimental).

Since it was established that under these last conditions too *N*-alkylation of **7** occurs in low extent, an alternative synthetic route to **3a** was envisaged. It would involve the use of the disulfide **4** (R_1 = $CH_2C_6H_5$) instead of 2,2'-dithiodianiline **4** (R_1 = H) in the reaction with ethyl acetoacetate carried out in chlorobenzene [2] or toluene at reflux [4] and with the absolute exclusion of acids. In this connection, it should be noted that if traces of *p*-toluenesulfonic acid are present the reaction leads to **5** and **6** in roughly equimolar amount instead of the compounds **7** and **8**, respectively. Therefore, the disulfide **4** (R^1 = $CH_2C_6H_5$) and ethyl acetoacetate (molar ratio 1:2) were allowed to react in toluene at reflux. So, the expected compounds **3a** and **12a** (Scheme 3) were obtained. The *N*-alkylacylketene *S,N*-acetal structure of **12a** was deduced by spectral means and confirmed by **12a** independent synthesis following a known procedure [5]. Moreover, it has been found that the outcome of the reaction of **4** (R^1 = $CH_2C_6H_5$) with ethyl acetoacetate did not change in the presence of catalytic amounts of *p*-toluenesulfonic acid, and that **3a** and **11a** are more readily formed in these last conditions, the progress of the reaction being monitored by tlc.

Once we obtained the desired compound **3a** in good yield (82%) we employed the same synthetic scheme to prepare a number of *N*-alkyl-2-acyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazines **3**. Thus, the reactions of *N,N'*-dialkyl dithiodianilines **4** with β-ketoesters **11**, of cyclic or acyclic type, were carried out in toluene containing *p*-toluenesulfonic acid as catalyst. In any case, a mixture of two products was obtained. By column chromatography it was pos-

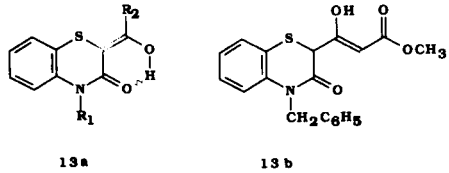
sible to isolate the corresponding *N*-alkyl-2-acyl-2*H*-1,4-benzothiazinone **3** and the *N*-alkylacylketene *S,N*-acetal **12** both in high yields. The reaction was also favourably extended to the β-ketoester **11** ($R_2 = CH_2COO\text{-}CH_3$, $R_3 = H$) containing a further ester function. In this last case the reaction proceeds faster and the corresponding compounds **3** and **12** were obtained being the additional ester function unaffected (Scheme 3).

Scheme 3



	R_1	R_2	R_3
a	$CH_2C_6H_5$	CH_3	H
b	$(CH_2)_3CH_3$	CH_3	H
c	$(CH_2)_2$	CH_3	H
d	$(CH_2)_4$	CH_3	H
e	$(CH_2)_3CH_3$	C_6H_5	H
f	$(CH_2)_4$	C_6H_5	H
g	$CH_2C_6H_5$	$-(CH_2)_3-$	
h	$CH_2C_6H_5$	$-(CH_2)_4-$	
i	$CH_2C_6H_5$	CH_2COOCH_3	H
j	$(CH_2)_3CH_3$	CH_2COOCH_3	H

The structures of the new compounds are fully supported by microanalytical and spectral data (Experimental). In particular, in the ^{1}H-nmr spectra of 2-monosubstituted compounds **3a-f,i,j** the presence of small amounts (< 10%) of the enol form **13a**, stabilized by an intramolecular hydrogen bond involving the lactam carbonyl, were detected. Moreover, in the case of **3i** the ^{1}H-nmr spectrum is complicated by the presence of further signals related to the enol form **13b**.

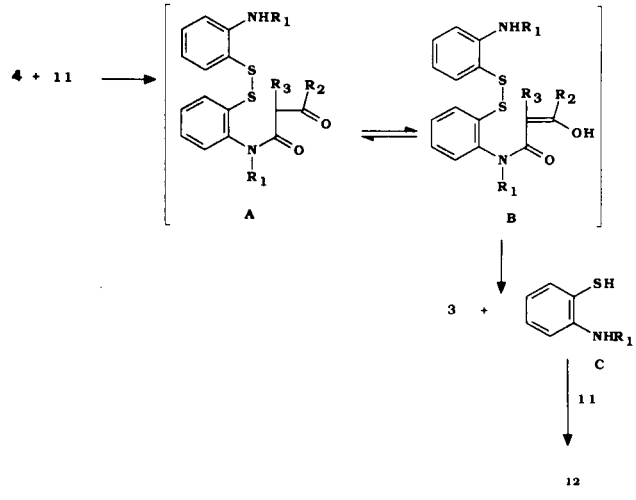


13a 13b

As for the stereochemistry at the carbon-carbon double bond of the enaminoketone moiety occurring in compounds **12** no conclusions have been reached by available spectral data reported in the Experimental.

A possible pathway accounting for the formation of the compounds **3** and **12** is depicted in Scheme 4. It involves the initial formation of an amide-disulfide intermediate **A** which in the corresponding enol form **B** give rise to 1,4-benzothiazine **3** together with the *N*-alkyl-2-aminobenzenethiol **C** by cleavage of disulfide bond. It could be consequent to a nucleophilic attack of the α-dicarbonyl carbon. Successively, formation of the compound **12** could occur by reaction of **C** with the B-ketoester **11**.

Scheme 4



In conclusion, a general method for preparing compounds of type **3** has been devised. By such a procedure the compounds **3** were obtained together with the *N*-alkyl acylketene *S,N*-acetals **12**. Finally, compounds of this last type are of interest as intermediates in the synthesis of heterocyclic compounds [6] and of cyanine dyes [7].

EXPERIMENTAL

Melting points were determined on a Buchi apparatus and are uncorrected. The ir spectra were taken on a Perkin-Elmer 283 infrared spectrophotometer. The ^{1}H nmr spectra were recorded on a Varian EM-390 instrument operating at 90 MHz. Chemical shifts are given in δ from tetramethylsilane as internal standard. Mass spectra were recorded on a Hewlett-Packard HP 5995C spectrometer. Analitical tlc were performed on Carlo Erba SI R_{254} silica gel plates. Column chromatography on silica gel (Merck 70-325 mesh) were carried out using light petroleum ether (bp 40-70°)-ethyl acetate (9:1 v/v) as eluent unless otherwise stated. Microanalyses were obtained using a Carlo Erba model 1106 analyser.

The yields are based on disulfide **4** used. All the reaction were carried out under nitrogen atmosphere. 2,2'-dithiodianiline compounds **4** (R_1 = H, Alkyl) were prepared according to literature procedures [8].

2-Acetyl-2-benzyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**9**).

A solution of 2-acetyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine **7**

[1] (0.40 g, 2 mmoles) in dry *N,N*-dimethylformamide (10 ml) at room temperature was treated in one portion with potassium *tert*-butoxide (0.25 g, 2 mmoles). The resulting mixture was stirred at room temperature for 15 minutes followed by the dropwise addition of benzyl bromide (0.35 g, 2 mmoles) in dry *N,N*-dimethylformamide (2 ml). Stirring was continued at room temperature for 1 hour and then the mixture was poured into ice water (150 ml) and acidified to *p*H 1 with 2*N* hydrochloric acid. Extraction with ethyl acetate (2 x 100 ml) followed by washing of the ethyl acetate extracts with water (2 x 100 ml), drying with sodium sulfate and removal of the solvent under reduced pressure gave an oil as the residue. The crude product was chromatographed on a silica gel column using light petroleum ether (40-70°) ethyl acetate (8:2) as eluent to give compound **9** as a white solid; yield, 0.51 g (85%), mp 153-154°; ir (potassium bromide): ν max = 1710, 1675 cm^{-1}, ^1H nmr (deuteriochloroform): δ 2.19 (s, 3H), 3.33 and 3.67 (2d, each 1H, J = 15 Hz), 6.7-7.5 (m, 9H), 9.55 (s, 1H); ms: m/z = 297 (M^+, 11), 255 (100).

Anal. Calcd. for $C_{17}H_{15}NO_2S$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.31; H, 5.10; N, 4.55.

By doubling the amount of potasssium *tert*-butoxide in the above procedure and following the same workup, the compounds **3a**, **9** and **10** were isolated in 20%, 5% and 45% yield, respectively.

2-Benzyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**10**).

The compound was obtained as pale yellow solid, mp 152-154° (from 2-propanol); ir (potassium bromide): ν max = 1665 cm^{-1}; ^1H nmr (deuteriochloroform): 2.80 (dd, 1H, J = 14 and 10Hz), 3.30 (dd, 1H, J = 10 and 5 Hz), 3.66 (dd, 1H, J = 10 and 5 Hz), 6.8-7.3 (m, 9H, ArH), 9.55 (s, bs, 1H); ms: m/z = 255 (M^+, 100).

Anal. Calcd. for $C_{15}H_{13}NOS$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.30; H, 5.20; N, 5.40.

General Procedure for the Reaction of 2,2'-Dithiodianilines **4** (R_1 = Alkyl) with β-Ketoesters **11**.

A solution of disulfide **4** (10 mmoles) and β-ketoester **11** (20 mmoles) in toluene (100 ml) containing catalytic amounts of *p*-toluenesulfonic acid was refluxed with stirring for the hours below reported (the reaction progress being monitored by tlc). The solvent was evaporated under reduced pressure and the resulting residue was chromatographed on silica gel column affording the compounds **3** and **12** in the order given.

N-Benzyl-2-acetyl-3-oxo-3,4-dihydro-2H-1,4-benzothiazine (**3a**).

This compound was obtained together with **12a** after 30 hours of reflux as a solid (82% yield), mp 117-119°; ir (potassium bromide): ν max = 1765, 1660 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.30 (s, 3H), 4.30 (s, 1H), 4.85 and 5.55 (2d, each 1H, J = 15 Hz), 6.8-7.4 (m, 9H), [small amounts (< 10%) of the enol form were detected]; ms: m/z = 297 (M^+, 27), 164 (100).

Anal. Calcd. for $C_{17}H_{15}NO_2S$: C, 68.67; H, 5.08; N, 4.71. Found: C, 68.37; H, 5.19; N, 4.61.

N-Benzyl-2-acetylmethylidene-2,3-dihydro-1,3-benzothiazole (**12a**).

This compound was obtained as a white solid (87% yield), mp 158-160°; ir (potassium bromide): ν max = 1610 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.13 (s, 3H), 5.20 (s, 2H), 5.90 (s, 1H), 6.9-7.6 (m, 9H); ms: m/z = 281 (M^+, 49), 91 (100).

Anal. Calcd. for $C_{17}H_{15}NOS$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.24; H, 5.40; N, 4.76.

Compound **12a** was obtained following a known procedure [5] to prepare *N*-alkyl acylketene *S,N*-acetals.

A mixture of 2-methylbenzothiazole (3 g, 20 mmoles and benzyl bromide (3.42 g, 20 mmoles) was heated at 80° with a water bath for 3 hours. The resulting *N*-benzyl-2-methylbenzothiazolium bromide (2.25 g, 7 mmoles) was suspended in dry pyridine (10 ml) and treated with acetyl chloride (0.6 ml, 6 mmoles). The suspension was stirred at room temperature for 1 hour. Then, the mixture diluted with water was extracted with chloroform (3 x 50 ml) and dried with sodium sulfate. Evaporation of the solvent under reduced pressure gave a crude solid which was crystallized from methanol to give 1.77 g of **12a** (90% yield).

N-Butyl-2-acetyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**3b**).

This compound was obtained together with **12b** after 17 hours of reflux as a solid (85% yield), mp 62-64° (light petroleum ether); ir (potassium bromide): ν max = 1720, 1665 cm^{-1}; ^1H nmr (deuteriochloroform): δ 0.93 (s, 3H), 1.1-1.8 (m, 4H), 2.25 (s, 3H), 3.9-4.1 (m, 2H), 4.20 (s, 1H), 6.9-7.4 (m, 4H), small amounts (< 10%) of enol form were detected]; ms m/z = 263 (M^+, 32), 221 (100).

Anal. Calcd. for $C_{14}H_{17}NO_2S$: C, 63.86; H, 6.51; N, 5.32. Found: C, 63.51; H, 6.71; N, 5.22.

N-Butyl-2-acetylmethylidene-2,3-dihydro-1,3-benzothiazole (**12b**).

This compound was obtained as a solid (85% yield), mp 99-100°; ir (potassium bromide): ν max = 1605 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.00 (t, 3H), 1.20-1.90 (m, 4H), 2.23 (s, 3H), 3.90 (m, 2H), 5.85 (s, 1H), 7.0-7.6 (m, 4H); ms: m/z = 247 (M^+, 19), 149 (100).

Anal. Calcd. for $C_{14}H_{17}NOS$: C, 67.99; H, 6.93; N, 5.66. Found: C, 68.08; H, 7.18; N, 5.61.

N-Cyclopentyl-2-acetyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**3c**).

This compound was obtained together with **12c** after 20 hours of reflux as a solid (80% yield), mp 80-82° (ethyl acetate-light petroleum ether); ir (potassium bromide): ν max = 1725, 1670 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.4-2.3 (m, 8H), 2.23 (s, 3H), 4.10 (s, 1H), 4.3-4.7 (m, 1H), 6.9-7.3 (m, 4H), small amounts (< 10%) of the enol form were detected]; ms: m/z = 275 (M^+, 38), 165 (100).

Anal. Calcd. for $C_{15}H_{17}NO_2S$: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.83; H, 6.48; N, 5.08.

N-Cyclopentyl-2-acetylmethylidene-2,3-dihydro-1,3-benzothiazole (**12c**).

This compound was obtained as a solid (85% yield), mp 104-106° (ethyl acetate-light petroleum ether); ir (potassium bromide): ν max = 1615 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.6-2.5 (m, 8H), 2.20 (s, 3H), 4.7-5.1 (m, 1H), 5.95 (s, 1H), 7.0-7.6 (m, 4H); ms: m/z = 259 (M^+, 19), 149 (100).

Anal. Calcd. for $C_{15}H_{17}NOS$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.69; H, 6.72; N, 5.34.

N-Cycloheptyl-2-acetyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**3d**).

This compound was obtained together with **12d** after 22 hours of reflux as oil (77% yield); ir (neat): ν max = 1715, 1660 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.4-2.6 (m, 12H), 2.23 (s, 3H), 4.12 (s, 1H), 4.2-4.6 (m, 1H), 6.8-7.4 (m, 4H), small amounts (< 10%) of

enol form were detected]; ms: m/z = 303 (M^+, 22), 165 (100).

Anal. Calcd. for $C_{17}H_{21}NO_2S$: C, 67.31; H, 6.98; N, 4.62. Found: C, 67.55; H, 7.16; N, 4.82.

N-Cycloheptyl-2-acetylmethylidene-2,3-dihydro-1,3-benzothiazole (**12d**).

This compound was obtained as a solid (96% yield), mp 100-101°; ir (potassium bromide): ν max = 1610 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.5-2.6 (m, 12H), 2.23 (s, 3H), 4.3-4.7 (m, 1H), 5.94 (s, 1H), 7.0-7.6 (m, 4H); ms: m/e = 287 (M^+, 20), 149 (100).

Anal. Calcd. for $C_{17}H_{21}NOS$: C, 71.05; H, 7.37; N, 4.87. Found: C, 71.45; H, 7.66; N, 4.82.

N-Butyl-2-benzoyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**3e**).

This compound was obtained together with **12e** after 7 hours of reflux as a yellow oil (95% yield); ir (neat): ν max = 1670 cm^{-1}; ^1H nmr (deuteriochloroform): δ 0.93 (t, 3H), 1.1-1.8 (m, 4H), 3.9-4.2 (m, 2H), 5.09 (s, 1H), 6.8-7.9 (m, 9H), [small amounts (< 10%) of enol form were detected]; ms: m/z = 325 (M^+, 35), 105 (100).

Anal. Calcd. for $C_{19}H_{19}NO_2S$: C, 70.14; H, 5.89; N, 4.31. Found: C, 70.42; H, 5.66; N, 4.42.

N-Butyl-2-benzoylmethylidene-2,3-dihydro-1,3-benzothiazole (**12e**).

This compound was obtained as a pale yellow solid (75% yield), mp 103-104°; ir (potassium bromide): ν max = 1600 cm^{-1}; ^1H nmr (deuteriochloroform): δ 0.97 (t, 3H), 1.2-1.9 (m, 4H), 4.60 (t, 2H), 6.53 (s, 1H), 7.0-8.1 (m, 9H); ms: m/z = 309 (M^+, 26), 105 (100).

Anal. Calcd. for $C_{19}H_{19}NOS$: C, 73.76; H, 6.19; N, 4.53. Found: C, 74.15; H, 6.50; N, 4.53.

N-Cycloheptyl-2-benzoyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**3f**).

This compound was obtained together with **12f** after 10 hours of reflux as a yellow oil (80% yield); ir (neat): ν max = 1660 cm^{-1} ^1H nmr (deuteriochloroform): δ 1.2-2.6 (m, 12H), 4.2-4.6 (m, 1H), 5.00 (s, 1H), 6.6-7.9 (m, 9H), [small amounts (< 10%) of enol form were detected]; ms: m/z = 365 (M^+, 23), 105 (100).

Anal. Calcd. for $C_{22}H_{23}NO_2S$: C, 72.31; H, 6.34; H, 3.83. Found: C, 72.45; H, 6.66; N, 3.82.

N-Cycloheptyl-2-benzoylmethylidene-2,3-dihydro-1,3-benzothiazole (**12f**).

This compound was obtained as a pale yellow solid (95% yield), mp 153-155° (ethanol); ir (potassium bromide): ν max = 1600 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.5-2.7 (m, 12H), 4.4-4.9 (m, 1H), 6.67 (s, 1H), 7.2-8.1 (m, 9H); ms: m/z = 349 (M^+, 23), 105 (100).

Anal. Calcd. for $C_{22}H_{23}NOS$: C, 75.62; H, 6.63; N, 4.01. Found: C, 75.45; H, 6.56; N, 4.12.

N-Benzyl-[2-spiro-2'-cyclopentan-1'-one]-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**3g**).

This compound was obtained together with **12g** after 31 hours of reflux as oil (85% yield); ir (neat): ν max = 1740, 1620 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.9-3.2 (m, 6H), 4.80 and 5.50 (2d, each 1H, J = 16 Hz), 6.7-7.3 (m, 9H); ms: m/z = 323 (M^+, 62), 91 (100).

Anal. Calcd. for $C_{19}H_{17}NO_2S$: C, 70.57; H, 5.30; N, 4.33. Found: C, 70.17; H, 5.54; N, 3.94.

N-Benzyl-2(2,3-dihydro-1,3-benzothiazole-2-ylidene)-1-cyclopentanone (**12g**).

This compound was obtained as solid (83% yield), mp 171-172° (ethanol); ir (potassium bromide): ν max = 1630 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.6-2.0 (m, 2H), 2.2-2.6 (m, 2H), 5.45 (s, 2H), 6.7-7.6 (m, 9H); ms: m/z = 307 (M^+, 61), 252 (100).

Anal. Calcd. for $C_{19}H_{17}NOS$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.45; H, 5.46; N, 4.82.

N-Benzyl-[2-spiro-2'-cyclohexan-1'-one]-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**3h**).

This compound was obtained together with **12h** after 20 hours of reflux as solid (60% yield), mp 159-160°(ethyl acetate-light petroleum ether); ir (potassium bromide): ν max = 1710, 1660 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.6-2.4 (m, 6H), 2.5-3.3 (m, 2H), 4.82 and 5.52 (2d, each 1H, J = 16 Hz), 6.8-7.5 (m, 9H); ms: m/z = 337 (M^+, 100).

Anal. Calcd. for $C_{20}H_{19}NO_2S$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.35; H, 5.82; N, 4.10.

N-Benzyl-2(2,3-dihydro-1,3-benzothiazole-2-ylidene)-1-cyclohexanone (**12h**).

This compound was obtained as pale yellow solid (50% yield), mp 146-148° (petroleum ether); ir (potassium bromide): ν max = 1585 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.3-2.0 (m, 4H), 2.50 (t, 2H), 2.81 (t, 2H), 5.50 (s, 2H), 6.7-7.6 (m, 9H); ms: m/z = 321 (M^+, 61), 202 (100).

Anal. Calcd. for $C_{20}H_{19}NOS$: C, 74.74; H, 5.96; N, 4.36. Found: C, 74.45; H, 5.68; N, 4.62.

N-Benzyl-2-methoxycarbonylacetyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**3i**).

This compound was obtained together with **12i** after 3 hours of reflux as oil (85% yield): ir (neat): ν max = 1745, 1720, 1670 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.70 (s, 3H), 3.73 (s, 2H), 4.66 (s, 1H), 4.90 and 5.55 (2d, each 1H, J = 16 Hz), 6.7-7.5 (m, 9H), small amounts (< 10%) of the enol form were detected; ms: m/z = 297 (34), 164 (100).

Anal. Calcd. for $C_{19}H_{17}NO_4S$: C, 64.22; H, 4.82; N, 3.94. Found: C, 64.12; H, 4.67; N, 3.85.

N-Benzyl-2-methoxycarbonylacetylidene-2,3-dihydro-1,3-benzothiazole (**12i**).

This compound was obtained as a pale yellow solid (74% yield), mp 138-139° (methanol); ir (potassium bromide): ν max = 1735, 1610 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.43 (s, 2H), 3.67 (s, 3H), 5.23 (s, 2H), 5.90 (s, 1H), 7.0-7.7 (m, 9H); ms: m/z = 281 (56), 91 (100).

Anal. Calcd. for $C_{19}H_{17}NO_3S$: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.51; H, 5.21; N, 4.13.

N-Butyl-2-methoxycarbonylacetyl-3-oxo-3,4-dihydro-2*H*-1,4-benzothiazine (**3j**).

This compound was obtained together with **12j** after 7 hours of reflux as oil (82% yield): ir (neat): ν max = 1745, 1720, 1670 cm^{-1}; ^1H nmr (deuteriochloroform): δ 0.94 (t, 3H), 1.0-1.8 (m, 4H), 3.70 (s, 3H), 3.73 (s, 2H), 3.8-4.1 (m, 2H), 4.53 (s, 1H), 6.9-7.4 (m, 4H), small amounts (< 10%) of enol form were detected]; ms: m/z = 263 (46), 221 (100).

Anal. Calcd. for $C_{16}H_{19}NO_4S$: C, 59.80; H, 5.96; N, 4.36. Found: C, 60.00; H, 5.87; N, 4.63.

N-Butyl-2-methoxycarbonylacetylidene-2,3-dihydro-1,3-benzothiazole (**12j**).

This compound was obtained as a pale yellow solid (74% yield), mp 95-96° (ethyl acetate-light petroleum ether); ir (potassium bromide): ν max = 1745, 1605 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.00 (t, 3H), 1.2-1.9 (m, 4H), 3.50 (s, 2H), 3.75 (s, 3H), 4.03 (t, 2H), 5.93 (s, 1H) 7.0-7.7 (m, 4H); ms: m/z = 247 (20), 149 (100).

Anal. Calcd. for $C_{16}H_{19}NO_3S$: C, 62.94; H, 6.27; N, 4.59. Found: C, 63.27; H, 6.23; N, 4.47.

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