Oxazepines and Thiazepines. 41 [1]. Synthesis of 4-Aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines by the Reaction of (*E,E*)-Cinnamylideneacetophenones with 2-Aminothiophenol and Their Conversion into 2,2-Disubstituted 3-Acetyl-2,3-dihydrobezothiazoles

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Dedicated to Professor Dr. Kálmán Hideg on the occasion of his 70th birthday.

New 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines **8-13** have been synthesized by an acid catalyzed reaction of 2-aminothiophenol (**1**) and (*E,E*)-cinnamylideneacetophenones **2-7**. Ring contraction of 1,5-benzothiazepines **8-13** provided 2,2-disubstituted 3-acetyl-2,3-dihydrobenzothiazoles **14-19** under acetylating conditions.

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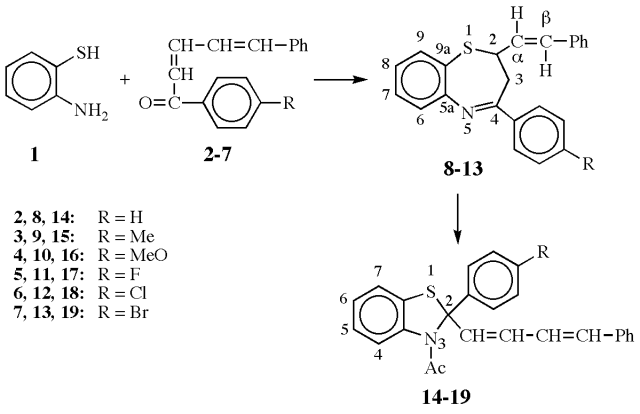
Owing to their well known bioactivities [1-9], the 1,5-benzothiazepines are especially important nitrogen- and sulfur-containing heterocyclic compounds in drug research. Synthesis and chemical transformations of various groups of benzothiazepines have been studied by numerous research groups, and the invented procedures have also been summarized in several review articles [10-14]. Because of their easy availability, 2,3-dihydro-1,5-benzothiazepines have received considerable attention. Most synthetic methods used for their preparation are based on the reaction of α,β-unsaturated ketones and 2-aminothiophenol [1,15-27]. Reaction of exocyclic α,β-unsaturated ketones with 2-aminothiophenol provided related tetracyclic benzothiazepines [28-34]. On all these bases, it can be concluded that the synthesis of benzothiazepines by the reaction of α,β-enones and 2-aminothiophenol is well established. However, the synthesis of 1,5-benzothiazepines by the reaction of the related α,β,γ,δ-unsaturated ketones with 2-aminothiophenol has not hitherto been published in the literature. For this reason, the major aim of our present paper is to describe our results on the synthesis of 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines by the reaction of (*E,E*)-cinnamylideneacetophenones with 2-aminothiophenol and the conversion of these 1,5-benzothiazepines into 2,2-disubstituted 3-acetyl-2,3-dihydrobenzothiazoles by their ring contraction under acylating reaction conditions.

(*E,E*)-Cinnamylideneacetophenones are known α,β,γ,δ-unsaturated ketones. Their parent compound, the 1,5-diphenylpenta-2,4-dien-1-one (**2**), was synthesized as early as 1895 [35]. Later, a wide variety of susbtituted derivatives have been described in the literature [36-42]. These unsaturated ketones are versatile intermediates for the synthesis of various heterocyclic compounds. The 2'-hydroxycinnamylideneacetophenones serve as starting materials for the preparation of variously substituted 2-styrylchromones and 3-styrylchromones [43-49]. Previously, we have synthesized 2-pyrazolines by the reaction of (*E,E*)-cinnamylideneacetophenones either with diazomethane [41] or with hydrazines [50]. Our present study is a newer utilization of the cinnamylideneacetophenones as intermediates for the synthesis of nitrogen-containing heterocyclic compounds.

Formerly we have investigated the reaction of the 2-aminothiophenol (**1**) with chalcones and related α,β-unsaturated ketones in detail. As a result, convenient procedures have been worked out for the synthesis of 2,4-disubstituted 2,3-dihydro-1,5-benzothiazepines [1,18-22,27]. It has been found that if the reaction was performed without an acid catalyst, in some cases the Michael adduct could be isolated depending on the electron density of the carbon-carbon double bond and/or on the bulkiness of the aryl groups of these α,β-unsaturated ketones. However, the utilization of an acid catalyst resulted in the formation of 2,4-disubstituted 2,3-dihydro-1,5-benzothiazepines in good yields irrespective of the structure elements of the starting α,β-unsaturated ketones.

Keeping our experiences in mind, (*E,E*)-cinnamylideneacetophenones **2**, **5** and **6** were allowed to react with 2-aminothiophenol (**1**) in hot ethanol (Method A) to try to isolate the appropriate Michael adducts. The course of the reaction was monitored by thin layer chromatography (tlc). When the starting (*E,E*)-cinnamylideneacetophenone disappeared

Scheme 1



after 6 hours reflux, a complex reaction mixture was obtained with several spots on the tlc plates. We have tried to separate the products by silica gel column chromatography. However, only the appropriate 4-aryl-2,3-dihydro-2-styryl-1,5-benzothaizepines **8**, **11** and **12** could be isolated in low yields (13-18%) in each case. In the course of the chromatographic separation, the column became dark brown indicating decomposition or polymerisation of some reaction products. This may account for the fact that only the stable 1,5-benzothiazepines **8**, **11** and **12** could be isolated in low yields.

To try to improve the yield of the preparation of the desired 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines, reaction of the (*E,E*)-cinnamylideneacetophenones **2-7** and 2-aminothiophenol (**1**) have been accomplished under acid-catalized reaction conditions as well. As a catalyst, trifluoroacetic acid proved to be convenient for the synthesis of 2,3-dihydro-1,5-benzothiazepines in many cases [27,32-34]. However, if it was used in this case, the reaction mixture became dark brown during less than 30 minutes reflux and an intractable reaction mixture was obtained. The use of *p*-toluenesulfonic acid catalyst resulted in the same experience. For this reason, relatively mild reaction conditions have been chosen to try to avoid the undesired side-reactions and/or decompositions. (*E,E*)-Cinnamylideneacetophenones **2-7** were allowed to react with 2-aminothiophenol (**1**) in hot ethanol in the presence of acetic acid catalyst (Method B) and 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines **8-13** were obtained in medium yields (38-53%). According to tlc monitoring, multicomponent reaction mixtures were obtained under these reaction conditions, too. Compounds **8-13** could only be isolated by silica gel column chromatography. The above-mentioned darkening of the columns were observed in these cases as well. Irrespective of the medium yields, previously unknown 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines became easily available in this way. It should also be mentioned that the electronic character of the substituent at the *p*-position of the phenyl ring is without influence on the course of the ring formation and on the yield of the isolated product. These compounds may serve as intermediates for the synthesis of valuable new 1,5-benzothiazepine derivatives.

Structures of all new 1,5-benzothiazepines **8-13** have been elucidated by elemental analyses, ir, ^{1}H and ^{13}C nmr spectroscopic measurements. In their ir spectra, a C=N band between 1600 and 1614 cm^{-1} is characteristic for a 2,3-dihydro-1,5-bezothiazepine skeleton [17-22,27]. ^{1}H NMR chemical shifts, multiplicity and coupling constant values (*cf.* Experimental) of protons attached to the C-2 and C-3 carbon atoms unequivocally prove the 2,3-dihydro-1,5-benzothiazepine structure. Coupling constant values of *ca.* 15 Hz indicate that the α-H and β-H protons of the styryl group are *trans*-oriented. In their ^{13}C nmr spectra, the chemical shifts of the aliphatic, the bridge-head and C-4 carbon atoms corroborate the presence of the above-mentioned heterocyclic ring.

Previously, we have found that 2,4-diaryl-2,3-dihydro-1,5-benzothiazepines [51-53] and the 4-aryl-2-(3-chromonyl)-2,3-dihydro-1,5-benzothiazepines [1] undergo a ring contraction under acylating conditions affording 2,2-disubstituted 3-acyl-2,3-dihydrobenzothiazoles. To provide newer examples for this transformation of the 2,3-dihydro-1,5-benzothiazepines invented by us [51], 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines **8-13** have also been utilized as starting materials to continue our former study.

Compounds **8-13** were allowed to react with a mixture of anhydrous pyridine and acetic anhydride (Method C) to afford 2,2-disubstituted 3-acetyl-2,3-dihydrobenzothiazoles **14-19** in relatively good (67-79%) yields. To try to improve these yields, 1,5-benzothiazepines **9** and **11-13** have also been reacted with acetic anhydride in the presence of triethylamine and 4-dimethylaminopyridine (Method D) which conditions previously proved to be beneficial for 2,4-diaryl-2,3-dihydro-1,5-benzothiazepines [52]. However, in the case of these 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines considerable decomposition might take place since all the crude reaction mixtures became almost black and the 2,2-disubstituted 3-acetyl-2,3-dihydrobenzothiazoles **15** and **17-19** obtained in this way could only be isolated in medium yields [46-52%]. Therefore, it appears that these stronger alkaline reaction conditions are adverse either to these 2-styryl-1,5-benzothiazepines or to the products of the ring contraction. Nonetheless, we have succeeded to utilize this ring contraction of the 2,3-dihydro-1,5-benzothiazepines for newer substrates to prove the generality of this ring contraction reaction to synthesize hitherto unknown 2,2-disubstituted 3-acetyl-2,3-dihydrobenzothiazoles.

Structure elucidation of new 2,2-disubstituted 3-acetyl-2,3-dihydrobenzothiazoles **14-19** has been performed by elemental analyses, ir, ^{1}H and ^{13}C nmr spectroscopies. In their ir spectra a characteristic C=O band unequivocally reveals the presence of an acetyl group. In the ^{1}H nmr spectra a broad singlet signal at around 2 ppm also proves the presence of an acetyl moiety. ^{1}H nmr signals of the butadienyl unit are overlapped by the aromatic proton signals. Their ^{13}C nmr spectra corroborate the 3-acetyl-2,3-dihydrobenzothiazole structure as well.

In summary, it can be concluded that we have managed to synthesize hitherto unknown 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines by the reaction of 2-aminothiophenol with (*E,E*)-cinnamylideneacetophenones. It means that these α,β,γ,δ-unsaturated ketones react with 2-aminothiophenol similarly to the related α,β-unsaturated ketones to afford 2,4-disubstituted 2,3-dihydro-1,5-benzothiazepines. It has also turned out that the 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines are convenient intermediates for the preparation of newer representatives of 2,2-disubstituted 3-acetyl-2,3-dihydroben-

zothiazoles by their ring contraction under acetylating reaction conditions.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H and ^{13}C nmr spectra were recorded on a Gemini 200 (at 200 and 50 MHz for ^{1}H and ^{13}C, respectively) at ambient temperature (*ca.* 20°) in chloroform-d with tetramethylsilane as the internal standard. Ir spectra were obtained in KBr pellets with a Perkin-Elmer 16 PC instrument. Elemental analyses were measured in house on a Carlo Erba 1106 EA instrument. The tlc was performed on Kieselgel 60 F_{254} (Merck) layer with 1,2-dichloroethane as eluent. The starting materials **2-7** were synthesized according to known procedures [35-42].

General Procedures for the Synthesis of 4-Aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines **8-13**

Method A.

A mixture of 2-aminothiophenol (**1**, 3.0 mmoles), (*E,E*)-cinnamylideneacetophenones (**2**, **5** and **6**, 2.5 mmoles) and ethanol (20.0 ml) was refluxed for 6 hours, the solvent was evaporated under reduced pressure and 1,5-benzothiazepines **8**, **11** and **12** were isolated by silica gel column chromatography with 1,2-dichloroethane as eluent.

Method B.

A mixture of 2-aminothiophenol (**1**, 6.0 mmoles), (*E,E*)-cinnamylideneacetophenone (**2-7**, 5.0 mmoles), acetic acid (5.0 ml) and ethanol (30.0 ml) was refluxed for 6 hours, then the solvent was evaporated under reduced pressure. Compounds **8-13** were isolated from the residue by silica gel column chromatography by using 1,2-dichloroethane as eluent.

2,3-Dihydro-4-phenyl-2-styryl-1,5-benzothiazepine (**8**).

This substance was prepared as pale yellow needles in 18% (Method A) and 53% (Method B) yields, mp 147-148°; ir: ν 1610 (C=N) cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.85 (1H, t, J = 12.7 Hz, 3-H), 3.20 (1H, dd, J = 12.8, 5.1 Hz, 3-H), 4.69 (1H, m, 2-H), 6.30 (1H, dd, J = 15.6, 8.5 Hz, α-H), 6.48 (1H, d, J = 15.6 Hz, β-H), 7.08-8.10 (m, 14 arom. H); ^{13}C nmr ($CDCl_3$): δ 35.5, 59.7, 122.6, 125.1, 125.3, 126.6, 127.6, 127.9, 128.2, 128.5, 128.7, 128.8, 129.3, 129.8, 130.1, 131.2, 135.3, 136.4, 152.5, 169.5.

Anal. Calcd. for $C_{23}H_{19}NS$: C, 80.91; H, 5.61; N, 4.10. Found: C, 80.95; H, 5.59; N, 4.13.

2,3-Dihydro-4-(4-methylphenyl)-2-styryl-1,5-benzothiazepine (**9**).

This compound was isolated as white needles in 48% (Method B) yield, mp 102-103°; ir: ν 1602 (C=N) cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.42 (3H, s, Me), 2.80 (1H, t, J = 12.9 Hz, 3-H), 3.17 (1H, dd, J = 12.8, 5.0 Hz, 3-H), 4.62 (1H, m, 2-H), 6.30 (1H, dd, J = 15.5, 8.3 Hz, α-H), 6.48 (1H, d, J = 15.6 Hz, β-H), 7.04-7.98 (m, 13 arom. H); ^{13}C nmr ($CDCl_3$): δ 21.3, 35.4, 59.7, 122.6, 124.9, 125.3, 126.7, 127.6, 127.9, 128.7, 129.3, 129.6, 129.9, 135.3, 135.5, 136.5, 141.6, 152.8, 169.2.

Anal. Calcd. for $C_{24}H_{21}NS$: C, 81.10; H, 5.96; N, 3.94. Found: C, 81.12; H, 5.98; N, 3.93.

2,3-Dihydro-4-(4-methoxyphenyl)-2-styryl-1,5-benzothiazepine (**10**).

This substance was prepared as white needles in 51% (Method B) yield, mp 150-151°; ir: ν 1600 (C=N) cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.82 (1H, t, J = 12.8 Hz, 3-H), 3.18 (1H, dd, J = 12.8, 5.3 Hz, 3-H), 3.89 (3H, s, OMe), 4.64 (1H, m, 2-H), 6.31 (1H, dd, J = 15.6, 8.7 Hz, α-H), 6.48 (1H, d, J = 15.6 Hz, β-H), 6.98-8.04 (m, 13 arom. H); ^{13}C nmr ($CDCl_3$): δ 35.3, 55.4, 59.6, 114.1, 122.6, 124.8, 125.3, 126.7, 127.9, 128.7, 129.3, 129.8, 130.3, 130.8, 135.3, 136.5, 152.9, 162.4, 168.5.

Anal. Calcd. for $C_{24}H_{21}NOS$: C, 77.61; H, 5.69; N, 3.77. Found: C, 77.64; H, 5.67; N, 3.75.

2,3-Dihydro-4-(4-fluorophenyl)-2-styryl-1,5-benzothiazepine (**11**).

This compound was obtained as white needles in 14% (Method A) and 38% (Method B) yields, mp 139-140°; ir: ν 1614 (C=N), cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.64 (1H, t, J = 12.9 Hz, 3-H), 3.18 (1H, dd, J = 12.9, 5.1 Hz, 3-H), 4.66 (1H, m, 2-H), 6.31 (1H, dd, J = 15.5, 8.6 Hz, α-H), 6.50 (1H, d, J = 15.6 Hz, β-H), 7.12-8.14 (m, 13 arom. H); ^{13}C nmr ($CDCl_3$): δ 35.4, 59.6, 115.9, 116.0, 122.5, 125.1, 125.3, 126.7, 128.0, 128.7, 129.5, 129.6, 129.8, 129.9, 134.4, 135.3, 136.4, 152.5, 168.1.

Anal. Calcd. for $C_{23}H_{18}FNS$: C, 76.86; H, 5.05; N, 3.89. Found: C, 76.84; H, 5.06; N, 3.91.

4-(4-Chlorophenyl)-2,3-dihydro-2-styryl-1,5-benzothiazepine (**12**).

This substance was isolated as yellow needles in 13% (Method A) and 44% (Method B) yields, mp 140-141°; ir: ν 1606 (C=N) cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.82 (1H, t, J = 13.1 Hz, 3-H), 3.14 (1H, dd, J = 13.2, 5.2 Hz, 3-H), 4.62 (1H, m, 2-H), 6.30 (1H, dd, J = 15.6, 8.6 Hz, α-H), 6.50 (1H, d, J = 15.6 Hz, β-H), 7.8-8.04 (m, 13 arom. H); ^{13}C nmr ($CDCl_3$): δ 35.4, 59.7, 122.6, 125.3, 126.7, 128.0, 128.7, 128.9, 129.1, 129.6, 129.9, 135.4, 136.4, 136.6, 137.4, 152.4, 168.2.

Anal. Calcd. for $C_{23}H_{18}ClNS$: C, 75.50; H, 4.83; N, 3.72. Found: C, 73.53; H, 4.85; N, 3.69.

4-(4-Bromophenyl)-2,3-dihydro-2-styryl-1,5-benzothiazepine (**13**).

This compound was prepared as yellow plates in 45% (Method B) yield, mp 129-130°, ir: ν 1606 (C=N) cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.83 (1H, t, J = 12.8 Hz, 3-H), 3.16 (1H, dd, J = 12.9, 5.1 Hz, 3-H), 4.64 (1H, m, 2-H), 6.30 (1H, dd, J = 15.7, 8.6 Hz, α-H), 6.51 (1H, J = 15.6 Hz, β-H), 7.09-7.97 (m, 13 arom. H); ^{13}C nmr ($CDCl_3$): δ 35.4, 59.8, 122.6, 125.3, 125.9, 126.7, 128.1, 128.7, 129.1, 129.6, 129.9, 132.0, 135.4, 136.4, 137.1, 152,4, 168.3.

Anal. Calcd. for $C_{23}H_{18}BrNS$: C, 65.72; H, 4.32; N, 3.33. Found: C, 65.68; H, 4.34; N, 3.31.

General Procedures for the Preparation of 2,2-Disubstituted 3-Acetyl-2,3-dihydrobenzothiazoles **14-19**.

Method C.

A mixture of 4-aryl-2,3-dihydro-2-styryl-1,5-benzothiazepines **8-13** (2.0 mmoles), acetic anhydride (10.0 ml) and anhydrous pyridine (5.0 ml) was stirred at 80° for 7 hours, then poured into water. The precipitate was separated by filtration, washed with water and recrystallized from methanol to afford substances **14-19**.

Method D.

4-Aryl-2,3-dihydro-2-styryl-1,5-benzothaizepines **9** and **11-13** (2.0 mmoles) were refluxed in a mixture of acetic anhydride (10.0 ml), triethylamine (5.0 ml) and 4-dimethylaminopyridine (0.5 g) for 3 hours, then poured into water. The precipitate was separated by filtration and purified by silica gel column chromatography to afford compounds **15** and **17-19**.

3-Acetyl-2,3-dihydro-2-phenyl-2-(4-phenyl-1,3-butadienyl)benzothiazole (**14**).

This compound was isolated as yellow needles in 73% (Method C) yield, mp 92-93°; ir: ν 1660 (C=O) cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.92 (3H, s, *Me*CO), 6.30-7.67 (m, 14 arom H. + 4H); ^{13}C nmr ($CDCl_3$): δ 25.9, 118.5, 121.8, 125.1, 125.4, 125.7, 126.4, 126.6, 127.0, 127.3, 127.5, 128.0, 128.4, 128.7, 129.3, 129.4, 131.4, 131.7, 134.8, 136.8, 139.5, 141.9, 170.5.

Anal. Calcd. for $C_{25}H_{21}NOS$: C, 78.31; H, 5.52; N, 3.65. Found: C, 78.27; H, 5.54; N, 3.67.

3-Acetyl-2,3-dihydro-2-(4-methylphenyl)-2-(4-phenyl-1,3-butadienyl)benzothiazole (**15**).

This substance was prepared as yellow needles in 71% (Method C) and 46% (Method D) yields, mp 107-108°; ir: ν 1670 (C=O) cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.91 (3H, s, *Me*CO), 2.38 (3H, s, Me), 6.36-7.57 (m, 13 arom. H + 4H); ^{13}C nmr ($CDCl_3$): δ 20.9, 25.9, 118.6, 121.8, 124.9, 125.4, 125.6, 126.3, 126.6, 127.3, 127.8, 128.0, 128.2, 128.7, 129.4, 131.0, 131.8, 134.7, 136.9, 138.6, 170.6.

Anal. Calcd. for $C_{26}H_{23}NOS$: C, 78.57; H, 5.83; N, 3.52. Found: C, 78.62; H, 5.81; N, 3.54.

3-Acetyl-2,3-dihydro-2-(4-mehoxyphenyl)-2-(4-phenyl-1,3-butadienyl)benzothiazole (**16**).

This compound was isolated as yellow plates in 72% (Method C) yield, mp 93-94°; ir: ν 1670 (C=O) cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.90 (3H, s, *Me*CO), 3.82 (3H, *Me*O), 6.29-7.64 (m, 13 arom. H + 4H); ^{13}C nmr ($CDCl_3$): δ 25.9, 55.2, 113.9, 118.7, 121.8, 125.1, 125.7, 126.6, 127.2, 127.3, 128.0, 128.7, 128.9, 130.9, 131.8, 133.5, 134.7, 136.9, 139.6, 159.8, 170.6.

Anal. Cald. For $C_{26}H_{23}NO_2S$: C, 75.53; H, 5.61; N, 3.39. Found: C, 75.56; H, 5.59; N, 3.41.

3-Acetyl-2,3-dihydro-2-(4-fluorophenyl)-2-(4-phenyl-1,3-butadienyl)benzothiazole (**17**).

This substance was obtained as yellow plates in 70% (Method C) and 51% (Method D) yields, mp 97-98°; ir: ν 1671 (C=O) cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.02 (3H, s, *Me*CO), 6.36-7.62 (m, 13 arom. H + 4H); ^{13}C nmr ($CDCl_3$): δ 25.7, 115.3, 118.4, 122.0, 125.2, 125.7, 126.5, 127.2, 127.9, 128.1, 128.8, 129.3, 129.6, 129.9, 131.6, 131.7, 134.9, 136.8, 170.4.

Anal. Calcd. for $C_{25}H_{20}FNOS$: C, 74.80; H, 5.02, N, 3.49. Found: C, 74.76; H, 5.04; N, 3.51.

3-Acetyl-2-(4-chlorophenyl)-2,3-dihydro-2-(4-phenyl-1,3-butadienyl)benzothiazole (**18**).

This compound was isolated as yellow plates in 79% (Method C) and in 48% (Method D) yields, mp 97-98°; ir: ν 1671 (C=O) cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.04 (3H, s, *Me*CO), 6.29-7.61 (m, 13 arom. H + 4H); ^{13}C nmr ($CDCl_3$): δ 25.7, 118.3, 122.1, 125.3, 125.8, 126.7, 127.2, 128.2, 128.8, 131.4, 132.0, 134.5, 135.1, 136.8, 139.2, 140.5, 169.8.

Anal. Calcd. for $C_{25}H_{20}ClNOS$: C, 71.85; H, 4.82; N, 3.35. Found: C, 71.89; H, 4.80; N, 3.34.

3-Acetyl-2-(4-bromophenyl)-2,3-dihydro-2-(4-phenyl-1,3-butadienyl)benzothiazole (**19**).

This substance was obtained as yellow plates in 67% (Method C) and 52% (Method D) yields, mp 111-112°; ir: ν 1671 (C=O) cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.07 (3H, s, *Me*CO), 6.37-7.52 (m, 13 arom. H + 4H); ^{13}C nmr ($CDCl_3$): δ 25.7, 118.3, 122.1, 122.7, 125.3, 125.8, 126.7, 127.2, 128.2, 128.8, 129.0, 131.3, 131.7, 132.0, 135.1, 136.8, 141.0, 170.0.

Anal. Calcd. for $C_{25}H_{20}BrNOS$: C, 64.94; H, 4.36; N, 3.03. Found: C, 64.97; H, 4.38; N, 3.01.

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