# Conversions of Thiochroman-4-ones into 1,2-Benzothiazepine, Benzo-[b]thiophen, and 1,2-Benzisothiazole Systems via Sulphimide Intermediates[1]

By Yasumitsu Tamura,* Yasushi Takebe, Said Mohamad M. Bayomi, Chisato Mukai, and Masazumi Ikeda, Faculty of Pharmaceutical Sciences, Osaka University, 133-1, Yamada-kami, Suita, Osaka, Japan
Masao Murase and Masahiro Kise, Research Laboratories, Nippon Shinyaku Co. Ltd., Nishinosho, Monguchi-cho, Kisshoin, Minami-ku, Kyoto, Japan

Reaction of thiochroman-4-ones (1a—g) with chloramine-T gave the corresponding N-tosylsulphimides (2a—g) and sulphoxides (5a—g). The N-tosylsulphimides (2a—d), on reaction with triethylamine in chloroform, gave 2-tosyl-2,3-dihydro-1,2-benzothiazepin-5(4H)-ones (3a—d), but the 2-methyl congeners (2e and f) yielded 2-crotonoyl-N-tosylbenzenesulphenamides (4e and f). When the reaction was carried out in acetonitrile, (2e and f) afforded (3e and f) and (Z)-2-ethylidene-2,3-dihydrobenzo[b]thiophen-3(2H)-ones (7e and f). The 2,2-dimethyl derivative (2g) led to only (4g) and (7g). Heating (2a—c) in acetic acid gave Diels–Alder dimers (6a—c) of 2-methylidene-2,3-dihydrobenzo[b]thiophen-3-ones, and (2e—g), upon heating in chloroform containing acetic acid, gave (7e—g). S-Amination of (1a, b, and d—f) with O-mesitylenesulphonylhydroxylamine followed by alkaline treatment gave 3-vinyl-1,2-benzisothiazoles (11a, b, and d—f).

PREVIOUSLY we described new entries into 1,2-benzothiazepine and 1,2-benzisothiazole systems from benzo[b]thiophen-3(2H)-ones through sulphimide intermediates.[2] We now report that such ring systems are also accessible from thiochroman-4-ones.

Thiochroman-4-one N-tosylsulphimides (2a—g) were prepared by the reaction of the corresponding thio-chroman-4-ones (1a—g) with chloramine-T trihydrate in methanol containing a small amount of acetic acid at 0 °C.† The reaction was accompanied by the formation of substantial amounts of the sulphoxides (5a—g). The



(1a-g)      (2a-g)      (3a-f)



(10a,b,d-f)      (11a,b,d-f)



(4e-g)      (5a-g)



(12)      (13)



(6a-c)      (7e-g)
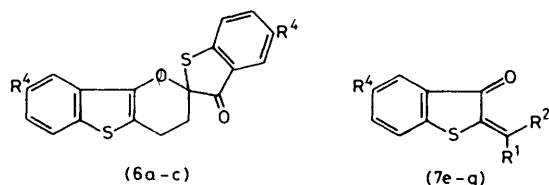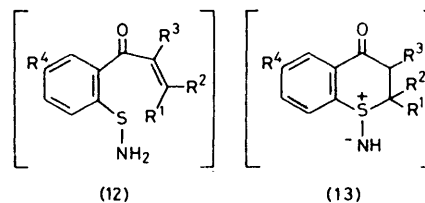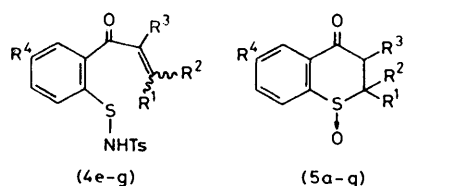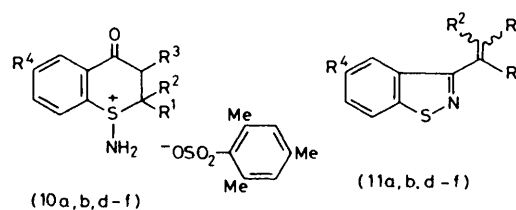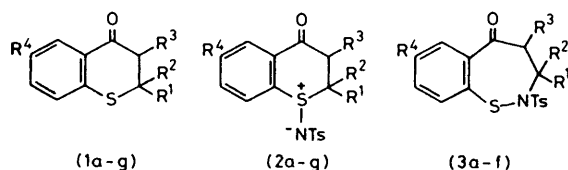
a; R¹=R²=R³=R⁴=H          e; R²=R³=R⁴=H, R¹=Me
b; R¹=R²=R³=H, R⁴=Me      f; R²=R³=H, R¹=R⁴=Me
c; R¹=R²=R³=H, R⁴=Cl      g; R³=R⁴=H, R¹=R²=Me
d; R¹=R²=R⁴=H, R³=Me



(8)      (9)
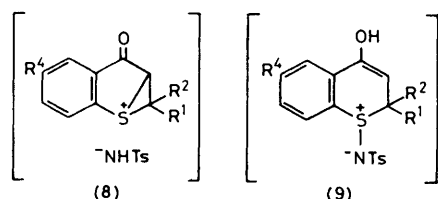
sulphimides could be separated by crystallisation from the crude reaction mixture. Column chromatography of the mother-liquor on silica gel gave the sulphoxides (5a—g) and small amounts of 2,3-dihydro-1,2-benzothiazepin-5(4H)-ones (3a—d) or sulphenamide derivatives (4e—g). These results are summarised in the Table. That (3a—d) and (4e—g) were produced from

† Although the N-tosylsulphimides (2a—c,f) have been described in a patent,[3] the m.p.s of (2a) and (2b) are incompatible with ours (see Experimental section).

Reaction of thiochroman-4-ones (1a—g) with
chloramine-T

Isolated yield (%)

| Compd. | (2) | (3) | (4) | (5) |
|---|---|---|---|---|
| (1a) | 53 | 2 | | 41 |
| (1b) | 54 | 5 | | 33 |
| (1c) | 40 | 1 | | 48 |
| (1d) | 43 | 15 | | 37 |
| (1e) | 55 | | 12 | 26 |
| (1f) | 62 | | 1 | 29 |
| (1g) | 85 | | 3 | 9 |

(2a—g) during the chromatography was demonstrated by the fact that (3) and (4) were not detected in the crude reaction mixture and that treatment of (2a) and (2e) with silica gel in chloroform at room temperature for 30 min gave (3a) and (4e), respectively, in high yield. The structures of the N-tosylsulphimides (2a—g) were confirmed by their spectral evidence (see Experimental section).

The N-tosylsulphimides (2) gave various compounds depending upon the structure of the substrate (particularly the number of the methyl substituent at the 2-position) and the reaction conditions (e.g. the solvent, acid, or base). Thus, when (2a—d) were treated with a catalytic amount of triethylamine in chloroform at room temperature for 1 h, the benzothiazepinones (3a—d) [2] were obtained in nearly quantitative yields. On the other hand, reaction of (2e) and (2f) under the identical conditions resulted in the formation of the corresponding sulphenamides (4e and f) in high yield. If the chloroform solution of the reaction mixture containing (4e) was allowed to stand for 24 h at room temperature, a mixture of (3e) (73%) and (Z)-2-ethylidenebenzo[b]thiophen-3(2H)-one (7e) * (17%) was obtained. The reaction proceeded more rapidly with the increase in the amount of triethylamine to give (3e) and (7e) in essentially the same ratio. When the reaction was performed in more a polar solvent such as acetonitrile, (2e) afforded a mixture of (3e) (34%) and (7e) (36%). Similarly (2f) afforded (3f) (52%) and (7f) † (40%). Treatment of (2g) with triethylamine in either chloroform or acetonitrile for 3 h gave products (4g) (45—50%) and (7g) (20—29%), and no 1,2-benzothiazepine (3g) was formed. The product ratio was dependent upon the reaction time: a longer reaction time resulted in an increase in the amount of (7g).

The formation of (3a—f) can be rationalised in terms of the intermediacy of the sulphenamides (4a—f), which may arise by β-elimination from (2a—f). An intramolecular Michael-type cyclisation leads to the observed products (3a—f). However, this step appears to be subject to steric retardation by the presence of the methyl group(s) at the β-position of the enone system, so

that an alternative intramolecular cyclisation to the thiiranium ions (8e—g) can compete with the above reaction: ring-opening reaction of (8e—g) affords (7e—g). Support for the proposed mechanistic schemes was obtained from the facts that (i) benzothiazepine (3e) was stable under the conditions used, suggesting that there is no equilibrium between (3e) and (4e) under these conditions, and (ii) treatment of the sulphenamide (4e) with triethylamine in acetonitrile gave (3e) and (7e) in essentially the same ratio as that seen in direct conversion of (2e).

The N-tosylsulphimides (2) took a different course of the reaction under acidic conditions. Thus, heating (2a) in acetic acid at 80° gave the spiro-compound (6a),[5] a Diels–Alder dimer of 2-methylenebenzo[b]thiophen-3(2H)-one (7a), in 72% yield. Similarly (2b and c) gave (6b and c) in 83 and 71% yields, respectively. The 2-methyl congeners (2e and f) and the 2,2-dimethyl derivative (2g) gave a complex mixture under these conditions but, upon heating in chloroform containing small amounts of acetic acid, the benzothiophenones (7e—g) were obtained in 25—29% yields.

The acid-catalysed ring contraction of (2) to (7) would involve again the thiiranium ions (8) which may arise from the sulphenamides (4). In fact, the ring-opening reaction of (2e) to (4e) was effected by stirring in chloroform in the presence of silica gel, and (4e) was converted to (7e) by refluxing in chloroform containing acetic acid. However, we can not eliminate the possibility that part of (7) is produced directly from (2) via the enols (9): this mechanism is closely related to that proposed for the ring contraction of (5g) to (7g) by treatment with acetic anhydride.[4]

The S-amination of (1a) was effected by treating with O-mesitylenesulphonylhydroxylamine [6] (MSH) in methylene chloride at room temperature. Treatment of the crude S-aminosulphonium salt (10a) with 10% sodium hydroxide at room temperature gave 3-vinyl-1,2-benzisothiazole (11a) in 38% overall yield. Similarly (1b and d—f) gave the corresponding 1,2-benziso-thiazoles (11b and d—f). The structure assignment of (11a, b, and d—f) is based on the spectroscopic data [2] (Experimental section).

A mechanistic rationalisation for the formation of (11) would involve the sulphenamide intermediates (12) which may arise through β-elimination of unisolable ' free ' sulphimides (13). Intramolecular condensation of the sulphenamide group of (12) with the carbonyl group leads to (11).

EXPERIMENTAL

N.m.r. spectra were determined with a Hitachi R-22 spectrometer (90 MHz; tetramethylsilane as internal standard). I.r. spectra were recorded with a Hitachi EPI-G2 spectrophotometer and u.v. spectra with a Hitachi 124 spectrophotometer. Low- and high-resolution mass spectra were obtained with Hitachi RMU-6E and RMU-6M instruments, respectively, with a direct inlet system operating at 70 eV. The elemental analyses and spectral data for (2b, c, and e—g), (3b, c, e, and f), (4f and g), (5b, c, and e—g),

---

* The Z-stereochemistry of (7e and f) was assigned by comparison of the chemical shift of the methyl group [δ 2.02 for (7e) and δ 2.04 for (7f)] with those of (7g) [δ 2.01 and 2.50 [4]]. Examination of a molecular model of (7g) suggests that the methyl group of the E-configuration should occur at the lower field than that of the Z-configuration due to the anisotropic effect of the carbonyl group at the 3 position.

(6b and c), (7f), and (11b, e, and f) are given in Supplementary Publication No. SUP 23005.*

Thiochroman-4-one (1a),[7] 6-methyl- (1b), [7] 6-chloro-(1c),[8] 3-methyl- (1d),[9] 2-methyl- (1e),[8,9] 2,6-dimethyl- (1f),[8] and 2,2-dimethyl-thiochroman-4-ones (1g) [10] were synthesised as described.

*Reaction of (1a—g) with Chloramine-T.*—The general procedure used is illustrated by the following example. A solution of chloramine-T trihydrate (4.90 g, 17.4 mmol) in MeOH (50 ml) was added dropwise to an ice-cooled solution of (1a) (2.60 g, 16 mmol) in MeOH (50 ml) containing acetic acid (0.1 ml). The mixture was stirred at 0 °C for 10 min and then at room temperature for 50 min. The solvent was removed under reduced pressure and the residue was dissolved in CHCl₃ (200 ml). The solution was washed with H₂O, dried (MgSO₄), and concentrated to give a brown residue which turned into a white crystalline solid upon addition of ether and MeOH. The solid was separated by filtration and recrystallised from MeOH and methylene chloride to give 1-(*p*-tolylsulphonylimino)thiochroman-4-one (2a) (2.80 g, 53%), m.p. 142—144 °C (lit.,[3] 97—98 °C) (Found: C, 57.6; H, 4.45; N, 3.95. Calc. for C₁₆H₁₅⁻NO₃S₂: C, 57.63; H, 4.53; N, 4.20%); $v_{max.}$ (KCl) 1 680 (C=O), 1 275, 1 135, 1 080 (SO₂), and 955 and 935 (S⁺–N⁻) cm⁻¹; δ (CDCl₃) 2.40 (3 H, s, toluene-ring CH₃), 2.7—4.0 (4 H, m, H-2 and -3), and 7.1—8.3 (8 H, m, aromatic). The filtrate was concentrated to give an oil which was chromatographed on silica gel. Elution with benzene–AcOEt (4 : 1 v/v) gave 2-*p-tolysulphonyl-2,3-dihydro*-1,2-*benzothiazepin*-5(4H)-*one* (3a) (102 mg, 2%), m.p. 121.5 °C (from MeOH) (Found: C, 57.75; H, 4.45; N, 4.0. C₁₆H₁₅NO₃S₂ requires C, 57.63; H, 4.53; N, 4.20%); $v_{max.}$ (KCl) 1 680 (C=O), 1 350, and 1 165 (SO₂) cm⁻¹; δ (CDCl₃) 2.26 (3 H, s, toluene-ring CH₃), 3.23 (2 H, m, H-4), 4.08 (2 H, m, H-3), and 6.8—7.7 (8 H, m, aromatic). Further elution with AcOEt gave 4-oxothiochroman S-oxide (5a) (1.16 g, 41%), identical (i.r. and n.m.r. spectra) with an authentic sample.[11] Similarly (1b) (2.0 g) gave 6-methyl-1-(*p*-tolylsulphonylimino)thiochroman-4-one (2b) (2.10 g, 54%), m.p. 145—146 °C (from MeOH–CH₂Cl₂) (lit.,[3] 132—134 °C), 7-*methyl*-2-*p-tolylsulphonyl-2,3-dihydro*-1,2-*benzothiazepin*-5(4H)-*one* (3b) (188 mg, 5%), m.p. 132.5 °C (from MeOH–CH₂Cl₂), and 6-methyl-4-oxothiochroman S-oxide (5b) (711 mg, 33%), m.p. 111—113 °C (from benzene–n-hexane) (lit.,[11] 110—111 °C). Compound (1c) (500 mg) gave 6-chloro-1-(*p*-tolylsulphonylimino)thiochroman-4-one (2c) (373 mg, 40%), m.p. 171—172 °C (from MeOH–CH₂Cl₂) (lit.,[3] 174—175 °C), 7-*chloro*-2-*p-tolylsulphonyl-2,3-dihydro*-1,2-*benzothiazepin*-5(4H)-*one* (3c) (9 mg, 1%), m.p. 170—171 °C (from MeOH), and 6-*chloro*-4-*oxothiochroman* S-*oxide* (5c) (260 mg, 48%), m.p. 103—104 °C (from benzene–n-hexane). Compound (1d) (1.84 g) gave 3-*methyl*-1-(p-*tolylsulphonylimino*)thiochroman-4-*one* (2d) (1.55 g, 43%), m.p. 144—146 °C (from MeOH–CH₂Cl₂), 4-methyl-2-*p*-tolylsulphonyl-2,3-dihydro-1,2-benzothiazepin-5(4H)-one (3d) (0.55 g, 15%), m.p. 102—103 °C (from MeOH) (lit.,[2] 102—103 °C), and 3-methyl-4-oxothiochroman S-oxide (5d) (0.75 g, 37%), m.p. 119—121 °C (from benzene–n-hexane) (lit.,[11] 116—117 °C). Compound (1e) (250 mg) gave 2-*methyl*-1-(p-*tolylsulphonyl-imino*)thiochroman-4-*one* (2e) (270 mg, 55%), m.p. 148—149 °C (from MeOH–CH₂Cl₂), 2-*crotonoyl*-N-(p-*tolylsulphonyl*)-*benzenesulphenamide* (4e) (56 mg, 12%), m.p. 138—139 °C (from diethyl ether) (Found: C, 58.8; H, 4.85; N,

* For details see Notice to Authors No. 7 *J. Chem. Soc., Perkin Trans. 1*, 1980, Index issue.

4.05. C₁₇H₁₇NO₃S₂ requires C, 58.76; H, 4.93; N, 4.03%); $v_{max.}$ (KCl) 3 200 (NH), 1 650 (C=O), 1 370, and 1 160 (SO₂) cm⁻¹; δ (CDCl₃) 1.98 (3 H, d, *J* 5.5 Hz, CH₃), 2.38 (3 H, s, toluene-ring CH₃), 6.00br (1 H, s, NH), and 6.9—8.15 (10 H, m, aromatic and vinylic), and 2-methyl-4-oxothiochroman S-oxide (5e) (70 mg, 26%), m.p. 111—112 °C (from benzene–n-hexane) (lit.,[11] 109—110 °C). Compound (1f) (5.0 g) gave 2,6-dimethyl-1-(*p*-tolylsulphonylimino)thiochroman-4-one (2f) (5.8 g, 62%), m.p. 169—170 °C (from MeOH–CH₂Cl₂) (lit.,[3] 168—169 °C), 2-*crotonoyl*-N-(p-*tolylsulphonyl*)benzenesulphenamide (4f) (58 mg, 1%), m.p. 152—154 °C (from diethyl ether), and 2,6-dimethyl-4-oxothiochroman S-oxide (5f) (1.57 g, 29%), m.p. 121—122 °C (from benzene–n-hexane) (lit.,[8] 97—98 °C). Compound (1g) (250 mg) gave 2,2-*dimethyl*-1-(p-*tolylsulphonylimino*)thiochroman-4-one (2g) (400 mg, 85%), m.p. 137—138 °C (from benzene–n-hexane), 2-(3-*methylcrotonoyl*)-N-(p-*tolylsulphonyl*)benzene-*sulphenamide* (4g) (15 mg, 3%), m.p. 129.5—130.5 °C (from di-isopropyl ether–n-hexane), and 2,2-dimethyl-4-oxothiochroman S-oxide (5g) (25 mg, 9%), m.p. 93—94 °C (from benzene–n-hexane) (lit.,[4] 92.5—93.5 °C).

*Reaction of the* N-*Tosylsulphimides* (2a—g).—(a) *Reaction in* CHCl₃ *in the presence of triethylamine.* A solution of (2a) (1.0 g, 3 mmol) in CHCl₃ (60 ml) containing triethylamine (0.1 ml) was stirred at room temperature for 1 h. The solution was washed with 10% HCl and H₂O, dried (MgSO₄), and concentrated to give an oil which crystallised upon the addition of MeOH. The solid was recrystallised from MeOH–CH₂Cl₂ to give (3a) (866 mg, 87%). In this manner (3b) (100%), (3c) (94%), and (3d) (100%) were obtained from the corresponding N-tosylsulphimides (2b—d). However, when this procedure was applied to (2e and f), (4e and f) were obtained in 84 and 100% yields, respectively. When the chloroform solution of the reaction mixture containing (4e) was allowed to stand for 24 h at room temperature, a mixture of (3e) (73%) and (7e) (17%) was obtained. (Z)-2-Ethylidenebenzo[*b*]thiophen-3(2H)-one (7e) was obtained as air-sensitive crystals (Found: M⁺, 178.0279. C₁₀H₈OS requires M, 178.0286), $v_{max.}$ (KBr) 1 680 (C=O) and 1 620 (C=C) cm⁻¹; δ (CDCl₃) 2.02 (3 H, d, *J* 7.5 Hz, CH₃), 7.13 (1 H, q, *J* 7.5 Hz, vinylic), and 7.05—7.85 (4 H, m, aromatic). Similar treatment of (2g) (200 mg) gave (4g) (90 mg, 45%) and 2-isopropylidenebenzo[*b*]thiophen-3(2H)-one (7g) (30 mg, 29%), m.p. 98—99 °C (lit.,[8] 102—103 °C), after separation by column chromatography on silica gel [benzene–AcOEt (4 : 1 v/v)].

(b) *Reaction in* CHCl₃ *in the presence of silica gel.* A mixture of (2a) (100 mg) and silica gel (2 g) in CHCl₃ (5 ml) was stirred at room temperature for 30 min. The mixture was filtered and concentrated to give (3a) (83 mg, 83%). Similar treatment of (2e) (300 mg) gave (4e) (290 mg, 96%).

(c) *Reaction in acetonitrile in the presence of triethylamine.* A solution of (2e) (1.0 g, 2.9 mmol) in acetonitrile (60 ml) containing triethylamine (0.1 ml) was stirred at room temperature for 3 h. The solvent was removed under reduced pressure and the residue was dissolved in CHCl₃. The solution was washed with 10% HCl and H₂O, dried (MgSO₄), and concentrated. The residue was chromatographed on silica gel. Elution with benzene gave (7e) (183 mg, 36%). Further elution with benzene–AcOEt (4 : 1 v/v) gave 3-*methyl*-2-*p-tolylsulphonyl-2,3-dihydro*-1,2-*benzothiazepin*-5(4H)-*one* (3e) (335 mg, 34%), m.p. 99—100 °C (from MeOH). In this manner, (Z)-2-*ethylidene*-5-*methylbenzo*[b]-*thiophen*-3(2H)-*one* (7f) (55 mg, 52%), air-sensitive crystals, and 3,7-*dimethyl*-2-p-tolylsulphonyl-2,3-dihydro-1,2-benzo-

*thiazepin*-5(4H)-*one* (3f) (80 mg, 40%), m.p. 145 °C (from MeOH), were obtained from (2f) (200 mg). Similar treatment of (2g) (100 mg) gave (4g) (50 mg, 50%) and (7g) (10 mg, 20%).

(d) *Reaction in acetic acid.* A solution of (2a) (100 mg) in acetic acid (5 ml) was heated at 80 °C for 4 h and then under reflux for 1 h and concentrated. The residue was chromatographed on silica gel (benzene) to give a dimer (6a) (35 mg, 72%); m.p. 170—171 °C (lit.,[5] 170—171 °C). Similarly, (2b) (200 mg) gave a dimer (6b) (85 mg, 83%), m.p. 152—154 °C (from MeOH). Compound (2c) (200 mg) gave a dimer (6c) (76 mg, 76%), m.p. 207—208 °C (from CHCl$_3$–MeOH).

(e) *Reaction in CHCl$_3$ in the presence of acetic acid.* A solution of (3e) (200 mg) in CHCl$_3$ (10 ml) containing acetic acid (1 ml) was refluxed for 6 h. After removal of solvent, the residue was passed through a short silica-gel column [benzene–AcOEt (4 : 1 v/v)] to give (7e) (30 mg, 29%). Similar treatment of (3f) (200 mg) gave (7f) (28 mg, 28%). Compound (3g) (150 mg) gave (7g) (20 mg, 25%).

*Cyclisation of* (4e) *to* (3e).—A solution of (4e) (500 mg) in acetonitrile (30 ml) containing triethylamine (0.1 ml) was stirred at room temperature for 3 h. Work-up gave (7e) (80 mg, 32%) and (3e) (151 mg, 30%).

*Conversion of* (4e) *to* (7e).—A solution of (4e) (100 mg) in CHCl$_3$ (5 ml) containing acetic acid (0.5 ml) was refluxed for 4 h. Work-up gave (7e) (36 mg, 70%).

*General Procedure for the* S-*Amination of* (1a, b, *and* d—f).—To an ice-cooled solution of a thiochroman-4-one (1) (10 mmol) in CH$_2$Cl$_2$ (40 ml) was slowly added a solution of MSH (15 mmol) in CH$_2$Cl$_2$ (15 ml) at room temperature. The mixture was stirred at room temperature for 1 h and diluted with ether to give the crystalline S-aminosulphonium mesitylenesulphonate which was washed with ether and used for the next reaction without further purification. The yields of the S-amine salts were 90% for (10a), 86% for (10b), 80% for (10d), 90% for (10e), and 90% for (10f).

*General Procedure for the Preparation of* 3-*Vinyl*-1,2-*benzisothiazoles* (11a, b, *and* d—f).—To an ice-cooled solution of the S-amine salt (10) (2.5 mmol) in CHCl$_3$ (100 ml) was added 10% NaOH solution (20 ml) at room temperature. The mixture was stirred at the same temperature for 10 min and filtered. The filtrate was washed with H$_2$O, dried (MgSO$_4$), and concentrated to give an oily product, which was purified either by distillation or by a short silica-gel column chromatography (benzene as eluant). 3-*Vinyl*-1,2-*benzisothiazole* (11a) (42%) was an oil (Found: $M^+$, 161.0317. C$_9$H$_7$NS requires $M$, 161.0299); $\lambda_{max.}$ (EtOH) 218, 227sh, 313, and 319 nm (log ε 4.41, 4.23, 3.76, and 3.82); δ (CDCl$_3$) 5.68 (1 H, dd, *J* 11 and 2 Hz, vinylic), 6.36 (1 H, dd, *J* 17 and 2 Hz, vinylic), 7.18 (1 H, dd, *J* 17 and 11 Hz, vinylic), and 7.35—8.2 (4 H, m, aromatic); 5-methyl-3-vinyl-1,2-benzisothiazole (11b) (35%) was an oil, b.p. 105 °C at 1 mmHg; 3-isopropenyl-1,2-benzisothiazole (11d) (30%) was an oil;[2] 3-(prop-1-enyl)-1,2-benzisothiazole (11e) (63%) was an oil, b.p. 103—105 °C at 1 mmHg; 5-methyl-3-(prop-1-enyl)-1,2-benzisothiazole (11f) (30%) was an oil.

REFERENCES

[1] Preliminary communication, Y. Tamura, S. M. Bayomi, C. Mukai, M. Ikeda, M. Murase, and M. Kise, *Tetrahedron Lett.*, 1980, 533.

[2] Y. Tamura, S. M. Bayomi, C. Mukai, M. Ikeda, and M. Kise, *J. Chem. Soc., Perkin Trans. 1*, in the press.

[3] K. Watanabe, T. Ishii, U. Shibata, and S. Seki, Jap. P. 74,101,379/1974 (*Chem. Abstr.*, 1975, **82**, 125281).

[4] R. B. Morin, D. O. Spry, and R. A. Mueller, *Tetrahedron Lett.*, 1969, 849.

[5] Y. Tamura, H. Ikeda, C. Mukai, S. M. Bayomi, and M. Ikeda, *Chem. Pharm. Bull.*, 1980, **28**, 430.

[6] Y. Tamura, J. Minamikawa, and M. Ikeda, *Synthesis* 1977, 1.

[7] F. Krollpfeiffer and H. Schultze, *Ber.*, 1923, **56**, 1819.

[8] F. Krollpfeiffer, H. Schultze, E. Schlumbohm, and E. Sommermeyer, *Ber.*, 1925, **58**, 1654.

[9] J. C. Petropoulos, M. A. McCall, and D. S. Tarbell, *J. Am. Chem. Soc.*, 1953, **75**, 1130.

[10] H.-J. Kurth, U. Kraatz, and F. Korta, *Liebigs Ann. Chem.*, 1977, 1141.

[11] I. W. Still, P. C. Arora, M. S. Chauhan, M.-H. Kwan, and M. T. Thomas, *Can. J. Chem.*, 1976, **54**, 455.