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Cationic Polar Cycloadditions of Phenylthionium Ions with Olefins: A New Route to Thiochromans

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Reaction of 2-chloro-*N*, *N*-dimethyl-2-(phenylthio)acetamide (**1a**) with styrene in the presence of stannic chloride gave 3,4-dihydro-*N*, *N*-dimethyl-4-phenyl-2*H*-1-benzothiopyran-2-carboxamide. The same benzothiopyran was also obtained from *N*, *N*-dimethyl-2-(phenylsulfinyl)acetamide and styrene under the Pummerer reaction conditions, but in lower yield. Similarly, α-chlorosulfides derived from ethyl 2-(phenylthio)acetate, 2-(phenylthio)acetonitrile, 1-(phenylthio)-2-propanone, and thioanisole reacted with styrene to give the corresponding 4-phenylbenzothiopyrans in variable yields. The reaction of **1a** with *trans*-stilbene gave the expected benzothiopyran derivative, but the reaction of **1a** with 1,1-diphenylethylene and phenylacetylene showed some variation of the reaction course. This cycloaddition reaction was extended to the intramolecular case. A possible mechanism for the formation of the benzothiopyran is discussed.

Keywords——cationic polar cycloaddition; thiochroman; benzothiopyran; intramolecular cycloaddition; Pummerer reaction; thionium ion

Cycloadditions with cationic compounds are well recognized as "cationic polar cycloadditions" and are classified in terms of the number of atoms involved in the cationic components such as $[4^+ + 2]$ and $[2^+ + 4]$ cycloadditions.[1] So far, reactions of this type have been investigated mainly with systems containing a nitrogen atom;[2] the cycloaddition with the sulfur-containing system has received little attention, the only reported example being the reaction of 1,3-dithienium fluoroborate with conjugated dienes to give the $[2^+ + 4]$ cycloadducts.[3] We now wish to describe both inter- and intra-molecular $[4^+ + 2]$ cycloadditions of phenylthionium ions with olefins,[4] which provide a novel route to the thiochroman (3,4-dihydro-2*H*-1-benzothiopyran) ring system.[5]

Results

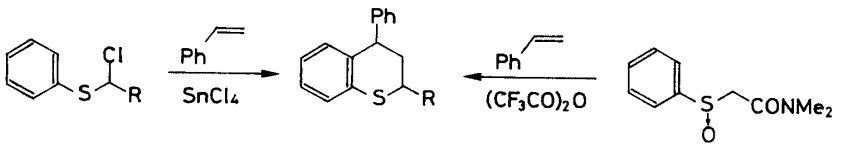
The cationic intermediates could be generated *in situ* from either the α-chlorosulfides or the sulfoxides. Thus, a solution of equimolar amounts of the α-chlorosulfide and the olefin was treated with 1 mol eq of stannic chloride in methylene chloride at 0 °C. The crude material was chromatographed to yield the thiochroman and by-products. In this manner, the α-chloroacetamide **1a** afforded the thiochroman **2a** in 72% yield when reacted with styrene. The same thiochroman **2a** was also obtained from the sulfinylacetamide **3** and styrene under the Pummerer reaction conditions, which involve successive treatment with trifluoroacetic anhydride and trifluoroacetic acid at 0 °C, but in lower yield (48%). The *cis*-stereochemistry of the adduct **2a** was readily deduced from the spin-coupling pattern of the C_2 and C_4 protons in the ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum; coupling constants of 10 and 5 Hz for the C_2 proton and 10 and 6 Hz for the C_4 proton indicate the C_2 and C_4 protons to be *cis*.

Similarly, the α-chloroacetate **1b** and styrene afforded an inseparable stereoisomeric mixture [7 : 3 by gas-liquid chromatography (GLC)] of adducts in 60% combined yield. The products were assigned the gross structure, ethyl 3,4-dihydro-4-phenyl-2*H*-1-benzothiopyran-2-carboxylate (**2b**). The ^{1}H-NMR spectrum using a shift reagent, europium tris(heptafluorobutanoylpivaloylmethanate) [Eu(fod)$_3$], indicated the major component of **2b** to have the *cis* configuration (see Experimental).

The reaction of the α-chloroacetonitrile **1c** with styrene gave the thiochroman **2c** as a stereoisomeric mixture (*cis* : *trans* = 7 : 3 by GLC and ^{1}H-NMR spectroscopy) in only 12% yield. The other products isolated were 2,2-bis(phenylthio)acetonitrile (**4**) (22%) and diphenyl disulfide (**5**) (5%), and the residue was polymeric in nature.

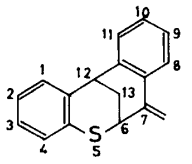
Interestingly, the α-chloroacetone **1d**, on treatment with styrene, gave one novel type of product **6** together with the thiochroman **2d** (*cis* : *trans* = 5 : 3 by ^{1}H-NMR spectroscopy). The structure of **6** was assigned on the basis of spectroscopic evidence. The elemental analysis and mass spectrum (MS) (M^+ *m/z* 250) showed the molecular formula to be $C_{17}H_{14}S$. The infrared (IR) spectrum of **6** showed the absence of the carbonyl group and the presence of the *exo*-methylene group (1630 and 890 cm^{-1}). In the ^{1}H-NMR spectrum, two *exo*-methylene protons appeared as singlets at δ 5.14 and 5.54, and the C_{13} protons appeared as part of an ABXY system with the AB portion centered at δ 2.36 with J_{AB} = 13 Hz, J_{AX} = 2 Hz, J_{AY} = 4 Hz, J_{BX} = 3 Hz, and J_{BY} = 5 Hz. The C_6 and C_{12} protons appeared as a multiplet centered at δ 4.25. The ^{13}C-NMR spectrum of **6** showed signals at δ 28.0 (C-13), 39.3, 41.5 (C-6 and C-12 or *vice versa*), 108.1 (C=$\underline{C}H_2$), and 145.9 (C-7). Compound **6** seems to be a secondary product formed by intramolecular cyclization of **2d**. In fact, the product ratio of **2d** and **6** was dependent on the reaction time; thus, shorter periods of time (3 h) resulted in isolation of **2d** and **6** in 19 and 22% yields, respectively, while only **6** was isolated in 60% yield when the reaction time was increased to 1 week.[6]

The reaction of the ω-chloroacetophenone **1e** with styrene did not give the cycloaddition product but only diphenyl disulfide, phenyl (phenylthio)methyl ketone, and unreacted starting material. Chloromethyl phenyl sulfide (**1f**) was found to react with styrene to give the thiochroman **2f** in 60% yield.



1a–f **2a–d,f** **3**

a : R=CONMe$_2$, b : R=CO$_2$Et, c : R=CN, d : R=COMe, e : R=COPh, f : R=H



$(PhS)_2CHCN$ $(PhS)_2$

4 **5** **6**

Chart 1

In order to check the generality of this reaction, we next examined the reaction of **1a** with some other olefins. Thus, treatment of **1a** and *trans*-stilbene with stannic chloride afforded a single adduct **7** in 39% yield. The adduct was assigned the all-*trans* stereochemistry because it exhibited large diaxial vicinal coupling constants for the C_2, C_3, and C_4 protons ($J_{2,3}$ = 9 Hz

and $J_{3,4}=10$ Hz). However, the reaction of **1a** with 1,1-diphenylethylene gave no thiochroman derivative but three products, a dimer of 1,1-diphenylethylene **8** (25%), a γ-lactone **9** (25%), and a Friedel–Crafts type product **10** (25%).

If acetylenes were used in the place of olefins, a new route to the 2*H*-1-benzothiopyrans might result. To this end, we have examined the reaction of **1a** with phenylacetylene. Under the same reaction conditions as described for the reaction with styrene, this reaction gave a rather complex mixture. Careful column chromatography of the mixture enabled us to isolate three products, benzothiopyran **11** (23%), a Friedel–Crafts type product **12** (13%), and a furan **13** (13%), whose structures were readily assigned on the basis of the spectroscopic evidence (see Experimental).

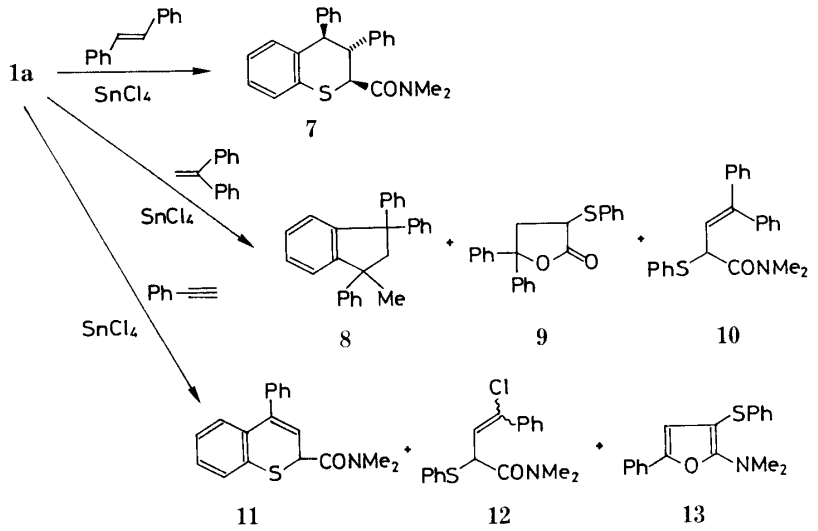


Chart 2

Finally, we applied this reaction to the intramolecular case. The starting material **15** was prepared by treatment of (phenylthio)acetyl chloride with *N*-allyl-*N*-methylamine in the presence of triethylamine followed by chlorination of the resulting sulfide **14** with *N*-chlorosuccinimide (NCS). Treatment of **15** with stannic chloride at 0 °C gave two products, **16** (24%) and **17** (32%). The structures of **16** and **17** were based on spectroscopic evidence (see Experimental). An attempt to cyclize **17** to **16** in the presence of stannic chloride was unsuccessful, indicating that **16** is the primary product of this reaction.

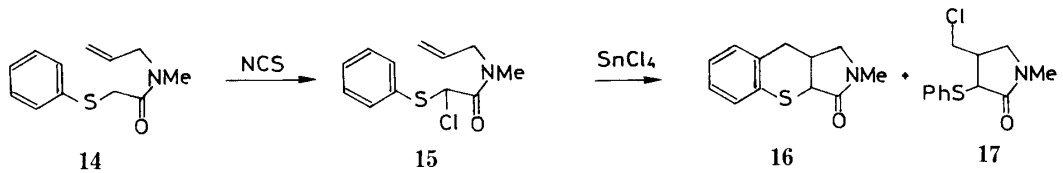
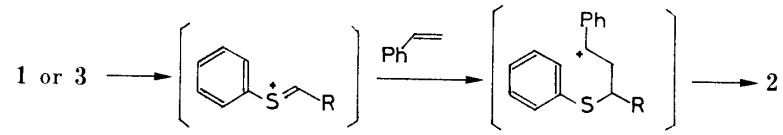


Chart 3

Discussion

The reaction of phenylthionium ions **18** generated from either α-chlorosulfides **1** or sulfoxide **3** with olefins to form the thiochromans **2** conforms to the concept of $[4^+ + 2]$ cycloaddition reactions, as proposed by Schmidt.[1] In principle, two mechanisms for the $[4^+ + 2]$ cycloaddition could be operative: (a) a concerted cycloaddition mechanism without

intermediates, or (b) a stepwise process. The process (a) is similar to that of the Diels–Alder reaction, and the latter process (b) involves attack of the electrophilic cation on the olefinic double bonds to form a new benzylic cation **19**, which undergoes cyclization by attack on the phenyl group. We prefer the latter two-step process for the following reasons. (i) All competing reactions can be well explained by the stepwise mechanism involving the cationic intermediates **19**: loss of a proton from the cations accounts for the formation of **10**,[7] intramolecular trapping of the cations by the carbonyl oxygen gives **9**[7] and **13**, and intermolecular trapping of the cations by the nucleophiles results in the formation of **12** and **17**. (ii) The observed selective regio- and stereo-chemistry can also be interpreted on the basis of the stepwise mechanism: the more stable cationic intermediates (benzylic cations) are always formed, and cyclization to the thiochromans takes place in such a way as to give the more stable stereoisomers (*cis*-**2a** and **7**).



18 19

Chart 4

Experimental[8]

Materials——*N*, *N*-Dimethyl-2-(phenylthio)acetamide,[9] ethyl 2-(phenylthio)acetate,[10] 2-(phenylthio)acetonitrile,[9] 1-(phenylthio)-2-propanone,[10] and phenyl (phenylthio)methyl ketone[10] were prepared as described in the literature. Thioanisole was obtained commercially.

General Procedure for Chlorination of Sulfides——NCS (1.42 g, 10.6 mmol) was added in portions during 20 min to a stirred solution of a sulfide (10.6 mmol) in carbon tetrachloride (30 ml) at 0 °C. The mixture was stirred at room temperature for 1 h. The precipitated succinimide was filtered off, and the filtrate was concentrated *in vacuo* below 20 °C. The crude material could be used for the next step without further purification. In this manner, the α-chlorosulfides **1a**—**e** and **15** were prepared from the corresponding sulfides. Chloromethyl phenyl sulfide (**1f**) was prepared in 70% yield from thioanisole and sulfuryl chloride,[11] bp 102—105 °C (12 mmHg) [lit.[11] bp 102—103 °C (12 mmHg)].

***N*, *N*-Dimethyl-2-(phenylsulfinyl)acetamide (3)**——A solution of sodium metaperiodate (0.36 g, 1.7 mmol) in water (10 ml) was added dropwise to a solution of *N*, *N*-dimethyl-2-(phenylthio)acetamide (0.33 g, 1.7 mmol) in methanol (5 ml). The mixture was stirred at room temperature for 1 d. The precipitated inorganic material was filtered off, and the filtrate was extracted with chloroform. The extract was dried ($MgSO_4$) and concentrated. The residue was chromatographed (silica gel; ethyl acetate) to give **3** (90%): mp 56—57 °C (from ethyl acetate–petroleum ether). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1035. ^{1}H-NMR ($CDCl_3$) δ: 2.75 (6H, s, NMe_2), 3.81, 3.97 (1H each, ABq, J=14 Hz, $SOCH_2$), 7.5—8.0 (5H, m, aromatic protons). *Anal.* Calcd for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63. Found: C, 56.80; H, 6.29; N, 6.70.

Reaction of 1a with Styrene (Procedure A)——The general procedure is illustrated in this example. Stannic chloride (0.23 ml, 2.0 mmol) was added dropwise at 0 °C under a nitrogen atmosphere to a solution of **1a** (460 mg, 2.0 mmol) and styrene (0.23 ml, 2.0 mmol) in methylene chloride (5 ml). The mixture was stirred at 0 °C for 1 h, diluted with water, and extracted with methylene chloride. The extract was washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed (silica gel; ethyl acetate) to give *cis*-3,4-dihydro-*N*, *N*-dimethyl-4-phenyl-2*H*-1-benzothiopyran-2-carboxamide (**2a**) (420 mg, 72%): mp 110—111 °C (from ether–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1645. ^{1}H-NMR ($CDCl_3$) δ: 2.3—2.8 (2H, m, C_3-H), 2.98, 3.17 (3H each, 2×s, NMe_2), 4.03 (1H, dd, J=10, 6 Hz, C_4-H), 4.37 (1H, dd, J=10, 5 Hz, C_2-H), 6.5—7.5 (9H, m, aromatic protons). MS *m/z*: 297 (M^+). *Anal.* Calcd for $C_{18}H_{19}NOS$: C, 72.69; H, 6.44; N, 4.71. Found: C, 72.45; H, 6.39; N, 4.81.

Reaction of 3 with Styrene (Procedure B)——Trifluoroacetic anhydride (150 mg, 0.73 mmol) was added dropwise at 0 °C to a solution of **3** (150 mg, 0.73 mmol) in methylene chloride (5 ml). The mixture was stirred at 0 °C for 40 min. The solvent was evaporated off *in vacuo*, and styrene (76 mg, 0.8 mmol) and then trifluoroacetic acid (3 ml) were added at 0 °C. This mixture was stirred at room temperature for 1 h, then diluted with water, and extracted with methylene chloride. The extract was washed with water, dried ($MgSO_4$), and concentrated. The residue was chromatographed (silica gel; benzene–ethyl acetate, 1 : 1) to give **2a** (105 mg, 48%).

Reaction of 1b with Styrene——Treatment of **1b** (240 mg, 1.0 mmol) with styrene (110 mg, 1.0 mmol) as described

in procedure A afforded, after work-up and chromatography (silica gel; benzene), ethyl 3,4-dihydro-4-phenyl-2*H*-1-benzothiopyran-2-carboxylate (**2b**) (195 mg, 60% as a *cis–trans* mixture) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1725. ^{1}H-NMR ($CDCl_3$) δ: 1.26 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.3—3.0 (2H, m, C_3-H), 4.13 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 3.9—4.5 (2H, m, C_2-H, C_4-H), 6.7—7.7 (8H, m, aromatic protons), 7.85—8.1 (1H, m, aromatic proton). The ^{1}H-NMR spectrum of **2b** (25 mg) in 0.4 ml of $CDCl_3$ in the presence of 15 mg of Eu(fod)$_3$ showed the following signals: δ 1.54 (t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.40 (ddd, J=14.5, 5.5, 4 Hz, C_3-H), 3.70 (dt, J=14.5, 11.5 Hz, C_3-H), 4.50 (dd, J=11.5, 5.5 Hz, C_4-H), 4.77 (q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.65 (dd, J=11.5, 4 Hz, C_2-H), 6.9—7.7 (m, aromatic protons), 8.35—8.6 (m, aromatic proton), which indicated the major isomer of **2b** to have *cis* configuration. The signals due to the *trans* isomer were too weak to be assigned. MS *m/z*: 298 (M^+). *Anal.* Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08. Found: C, 72.57; H, 6.07. GC-MS analysis of this mixture showed two peaks (ratio 7 : 3) and the MS fragmentation patterns of these peaks were essentially identical.

Reaction of 1c with Styrene——Treatment of **1c** (684 mg, 3.7 mmol) with styrene (387 mg, 3.7 mmol) as described in procedure A afforded, after work-up and chromatography (silica gel; *n*-hexane–benzene, 1 : 1), diphenyl disulfide (**5**) (19 mg, 5%), mp 60—61 °C (lit.,[12] 60—61 °C), 2,2-di(phenylthio)acetonitrile (**4**) (106 mg, 22%), and 3,4-dihydro-4-phenyl-2*H*-1-benzothiopyran-2-carbonitrile (**2c**) (111 mg, 12% as a *cis–trans* mixture).

Compound **4**: An oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2230 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 4.82 (1H, s, CHCN), 6.5—7.8 (10H, m, aromatic protons). Exact MS *m/z*: Calcd for $C_{14}H_{11}NS_2$: 257.0330. Found: 257.0315.

Compound **2c**: mp 107—108 °C (from ethyl acetate–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2240. ^{1}H-NMR ($CDCl_3$) δ: 2.1—3.0 (2H, m, C_3-H), 3.8—4.5 (2H, m, C_2-H, C_4-H), 6.5—7.7 (9H, m, aromatic protons). The ^{1}H-NMR spectrum of **2c** (65 mg) in 0.4 ml of $CDCl_3$ in the presence of 15 mg of Eu(fod)$_3$ showed the following signals: δ 2.15—3.05 (m, C_3-H), 4.03 (dd, J=10, 4.5 Hz, C_4-H), 4.32 (dd, J=9.5, 6 Hz, C_2-H), 6.5—7.7 (m, aromatic protons), which indicated the major isomer of **2c** to have *cis* configuration. The signals due to the *trans* isomer were too weak to be assigned. MS *m/z*: 251 (M^+). *Anal.* Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57. Found: C, 76.16; H, 5.01; N, 5.65. GLC analysis of the crude product showed it to be an isomeric mixture in a ratio of 7 : 3.

Reaction of 1d with Styrene——Treatment of **1d** (2.14 g, 12.9 mmol) with styrene (1.34 g, 12.9 mmol) as described in procedure A gave, after work-up and chromatography (silica gel; *n*-hexane–benzene, 1 : 1), 2-acetyl-3,4-dihydro-4-phenyl-2*H*-1-benzothiopyran (**2d**) (666 mg, 19%) and 7,12-dihydro-7-methylene-6,12-methano-6*H*-dibenzo[*b*,*e*]thiocin (**6**) (772 mg, 22%).

Compound **2d**: An oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1715. ^{1}H-NMR ($CDCl_3$) δ: 2.1—2.6 (2H, m, C_3-H), 2.20, 2.25 (3H, 5 : 3, 2×s, $COCH_3$), 3.6—4.5 (2H, m, C_2-H, C_4-H), 6.5—7.6 (9H, m, aromatic protons). The ^{1}H-NMR spectrum of **2d** (40 mg) in 0.4 ml of $CDCl_3$ in the presence of 35 mg of Eu(fod)$_3$ showed the following signals: δ 3.55—3.95 (2H, m, C_3-H due to *cis* and *trans* isomers), 3.85 (5/8×3H, s, $COCH_3$ due to *cis* isomer), 4.13 (3/8×3H, s, $COCH_3$ due to *trans* isomer), 4.60 (5/8H, dd, J=9.5, 6 Hz, C_4-H due to *cis* isomer), 4.99 (3/8H, t, J=5 Hz, C_4-H due to *trans* isomer), 5.37 (5/8H, dd, J=9, 5.5 Hz, C_2-H due to *cis* isomer), 6.02 (3/8H, dd, J=9, 7 Hz, C_2-H due to *trans* isomer). Exact MS *m/z*: Calcd for $C_{17}H_{16}OS$: 268. 0942. Found: 268.0932.

Compound **6**: mp 107—108 °C (from methanol). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1630, 890. ^{1}H-NMR ($CDCl_3$) δ: 2.36 (2H, m, C_{13}-H), 4.25 (2H, m, C_6- and C_{12}-H), 5.14, 5.54 (1H each, 2×s, $=CH_2$), 6.8—7.8 (10H, m, aromatic protons). ^{13}C-NMR ($CDCl_3$), δ: 28.0 (t, C-13), 39.3 (d, C-6 or C-12), 41.5 (d, C-12 or C-6), 108.1 (t, $C=\underline{C}H_2$), 123.8 (d), 124.8 (d), 125.5 (d), 126.5 (d), 126.9 (d), 128.4 (d), 128.6 (d), 129.2 (d), 131.3 (s), 132.4 (s), 137.2 (s), 137.4 (s) (aromatic carbons), 145.9 (s, C-7). MS *m/z*: 250 (M^+). *Anal.* Calcd for $C_{17}H_{14}S$: C, 81.60; H, 5.60. Found: C, 81.19; H, 5.60.

Reaction of 1f with Styrene—Treatment of **1f** (260 mg, 1.7 mmol) with styrene (170 mg, 1.7 mmol) as described in procedure A afforded 3,4-dihydro-4-phenyl-2*H*-1-benzothiopyran (**2f**) (229 mg, 60%) as an oil. ^{1}H-NMR ($CDCl_3$) δ: 2.2—2.45 (2H, m, C_3-H), 2.7—3.2 (2H, m, C_2-H), 4.20 (1H, dd, J=10, 4 Hz, C_4-H), 6.8—7.6 (9H, m, aromatic protons). *Anal.* Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23. Found: C, 79.34; H, 6.12.

Reaction of 1a with *trans*-Stilbene——Treatment of **1a** (400 mg, 1.75 mmol) with *trans*-stilbene (315 mg, 1.75 mmol) as described in procedure A afforded 3,4-dihydro-*N*,*N*-dimethyl-*t*-3,*c*-4-diphenyl-2*H*-1-benzothiopyran-*r*-2-carboxamide (**7**) (257 mg, 39%): mp 174—175 °C (from *n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1635. ^{1}H-NMR ($CDCl_3$) δ: 2.74, 2.90 (3H each, 2×s, NMe_2), 3.88 (1H, dd, J=10, 9 Hz, C_3-H), 4.30 (1H, d, J=10 Hz, C_4-H), 4.52 (1H, d, J=9 Hz, C_2-H), 6.6—7.3 (14H, m, aromatic protons). MS *m/z*: 373 (M^+). *Anal.* Calcd for $C_{24}H_{23}NOS$: C, 77.18; H, 6.21; N, 3.75. Found: C, 77.13; H, 6.29; N, 4.03.

Reaction of 1a with 1,1-Diphenylethylene——Treatment of **1a** (2.0 g, 8.7 mmol) with 1,1-diphenylethylene (1.6 g, 8.7 mmol) as described in procedure A afforded a mixture consisting of three products, which were separated by chromatography (silica gel; *n*-hexane–ethyl acetate, 3 : 1) to give 3-methyl-1,1,3-triphenylindan (**8**) (394 mg, 25%), mp 142—143 °C (lit.,[13] mp 143 °C), 4,4-diphenyl-2-(phenylthio)-4-butanolide (**9**) (765 mg, 25%), and *N*,*N*-dimethyl-4,4-diphenyl-2-(phenylthio)-3-butenamide (**10**) (896 mg, 25%).

Compound **9**: mp 119.5—120 °C (from ethyl acetate–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1775. ^{1}H-NMR ($CDCl_3$) δ: 2.77 (1H, dd, J=13, 11 Hz, C_3-H), 3.40 (1H, dd, J=13, 8 Hz, C_3-H), 3.93 (1H, dd, J=11, 8 Hz, C_2-H), 7.0—7.7 (15H, m, aromatic protons). *Anal.* Calcd for $C_{22}H_{18}O_2S$: C, 76.27; H, 5.24. Found: C, 76.07; H, 5.11.

Compound **10**: mp 97—97.5 °C (from ethyl acetate–*n*-hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640. ^{1}H-NMR ($CDCl_3$) δ: 2.72, 2.92 (3H each, 2×s, NMe_2), 4.60 (1H, d, J=10 Hz, C_2-H), 6.47 (1H, d, J=10 Hz, C_3-H), 6.6—7.5 (15H, m, aromatic

protons). *Anal.* Calcd for $C_{24}H_{23}NOS$: C, 77.18; H, 6.21; N, 3.75. Found: C, 77.30; H, 6.14; N, 3.79.

Reaction of 1a with Phenylacetylene——Treatment of **1a** (1.0 g, 4.5 mmol) with phenylacetylene (0.46 g, 4.5 mmol) as described in procedure A afforded many products, which were separated by careful chromatography (silica gel; benzene–ethyl acetate, 5 : 1) to give *N*,*N*-dimethyl-4-phenyl-2*H*-1-benzothiopyran-2-carboxamide (**11**) (305 mg, 23%), 4-chloro-*N*,*N*-dimethyl-4-phenyl-2-(phenylthio)-3-butenamide (**12**) (197 mg, 13%), and 2-(*N*,*N*-dimethylamino)-5-phenyl-3-(phenylthio)furan (**13**) (174 mg, 13%).

Compound **11**: mp 164—165 °C (from ethyl acetate–petroleum ether). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640. ^{1}H-NMR ($CDCl_3$) δ: 3.01, 3.15 (3H each, 2×s, NMe_2), 4.78 (1H, d, J=5 Hz, C_2-H), 6.12 (1H, d, J=5 Hz, C_3-H), 7.0—7.5 (9H, m, aromatic protons). *Anal.* Calcd for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74. Found: C, 72.73; H, 5.70; N, 4.95.

Compound **12**: An oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640. ^{1}H-NMR ($CDCl_3$) δ: 2.76, 2.98 (3H, 1 : 6, 2×s, NMe), 2.91, 3.10 (3H, 1 : 6, 2×s, NMe), 4.50, 5.14 (1H, 1 : 6, 2×d, J=11 and 10 Hz, respectively, C_2-H), 6.36, 6.52 (1H, 1 : 6, 2×d, J=11 and 10 Hz, respectively, C_3-H), 7.1—7.8 (10H, m, aromatic protons). Exact MS *m/z*: Calcd for $C_{18}H_{18}ClNOS$: 333.0766 and 331.0784. Found: 333.0750 and 331.0766.

Compound **13**: An oil. ^{1}H-NMR ($CDCl_3$) δ: 2.95 (6H, s, NMe_2), 6.40 (1H, s, C_4-H), 6.9—7.7 (10H, m, aromatic protons). Exact MS *m/z*: $C_{18}H_{17}NOS$: 295.1029. Found: 295.1016.

***N*-Allyl-*N*-methyl-2-(phenylthio)acetamide (14)**——A solution of 2-(phenylthio)acetyl chloride (4.43 g, 23.7 mmol) in methylene chloride (10 ml) was added dropwise at 0 °C to a solution of *N*-allyl-*N*-methylamine (1.85 g, 26 mmol) and triethylamine (2.64 g, 26 mmol) in methylene chloride (30 ml). The mixture was stirred at 0 °C for 1 h and diluted with water (20 ml). The organic layer was separated and the aqueous layer was extracted with methylene chloride. The combined extract was washed with brine, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed (silica gel; ethyl acetate) to give **14** (4.87 g, 93%) as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1635. ^{1}H-NMR($CDCl_3$) δ: 2.92, 2.98 (3H, 1 : 1, 2×s, NMe), 3.73, 3.75 (2H, 1 : 1, 2×s, SCH_2), 3.8—4.1 (2H, m, NCH_2), 4.8—6.0 (3H, m, $CH=CH_2$), 7.1—7.6 (5H, m, aromatic protons). *Anal.* Calcd for $C_{12}H_{15}NOS$: C, 65.12; H, 6.83; N, 6.33. Found: C, 64.90; H, 6.71; N, 6.38.

Cyclization of 15——Essentially the same procedure as described in procedure A was used. Stannic chloride (0.15 ml, 1.27 mmol) was added dropwise under a nitrogen atmosphere, to a solution of **15** (325 mg, 1.27 mmol) in methylene chloride (5 ml) at 0 °C. The mixture was stirred at 0 °C for 1 h, then diluted with water. Work-up and chromatography (silica gel; ethyl acetate) gave 2-methyl-1,2,9,9a-tetrahydro[1]benzothiopyrano[2,3-*c*]pyrrol-3(3a*H*)-one (**16**) (67 mg, 24%) and 4-chloromethyl-*N*-methyl-3-(phenylthio)pyrrolidin-2-one (**17**) (104 mg, 32%).

Compound **16**: mp 163—164 °C (from ethanol). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680. ^{1}H-NMR ($CDCl_3$) δ: 2.7—3.1 (3H, m, C_9- and C_{9a}-H), 2.92 (3H, s, NMe), 3.24 (1H, t, J=10 Hz, one of C_1-H), 3.56 (1H, dd, J=7, 10 Hz, one of C_1-H), 3.70 (1H, br d, J=12 Hz, C_{3a}-H), 6.9—7.2 (4H, m, aromatic protons). MS *m/z*: 219 (M^+). *Anal.* Calcd for $C_{12}H_{13}NOS$: C, 65.72; H, 5.97; N, 6.39. Found: C, 65.47; H, 5.97; N, 6.46.

Compound **17**: An oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685, ^{1}H-NMR ($CDCl_3$) δ: 2.45—3.0 (1H, m, C_4-H), 2.80 (3H, s, NMe), 3.18 (2H, d, J=7 Hz, $ClCH_2$), 3.5—3.7 (3H, m, C_3- and C_5-H), 7.1—7.7 (5H, m, aromatic protons), MS *m/z*: 255 (M^+). *Anal.* Calcd for $C_{12}H_{14}ClNOS$: C, 56.35; H, 5.52; N, 5.48. Found: C, 55.97; H, 5.47; N, 5.56.

References and Notes

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7) In the reaction of **1a** with diphenylethylene, the approach of the phenylthio group to the benzylic cationic center formed is apparently hindered by the two phenyl groups.
8) All melting points are uncorrected. NMR spectra were determined with a Hitachi R-22 (90 MHz) spectrometer (tetramethylsilane as an internal standard). IR spectra were recorded with JASCO IRA-1 and A-100 spectrophotometers. High- and low-resolution mass spectra were obtained with a Hitachi M-80 instrument at 20 eV. GLC was carried out on a Shimadzu GC-5APTF gas chromatograph using a 1 m×3 mm i.d. glass column of 3% OV-17 on Chromosorb W.
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