Synthesis of 2,6-Diphenyl-3-formyl-4*H*-thiopyran-4-one and Related Compounds

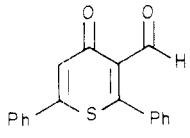
Chin H. Chen* and George A. Reynolds

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

Received February 22, 1979

The title compound **1** was prepared by an unusual selenium dioxide oxidation of 4-chloro-2,6-diphenyl-3-formyl-2*H*-thiopyran (**11**) which was obtained either by treating 2,6-diphenyl-4*H*-dihydrothiopyran-4-one (**10**) with $POCl_3$/DMF or preferably by allowing $POCl_3$ to react with the dimethylamine derivative **15**. The latter compound was prepared in good yield from **10** and the dimethyl acetal of DMF. Alternatively, **1** was synthesized by acetolysis of **15** in the presence of a catalytic amount of sulfuric acid to give a good yield of 2,6-diphenyl-3-formyl-4*H*-2,3-dihydrothiopyran-4-one (**16**), which was readily dehydrogenated under normal conditions with selenium dioxide.

In the course of synthesizing new donors based on phenyl-substituted thiopyrans which were to be used to prepare organic conductors,[1] we required 2,6-diphenyl-3-formyl-4*H*-thiopyran-4-one (**1**) as a key intermediate.



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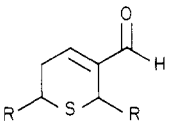
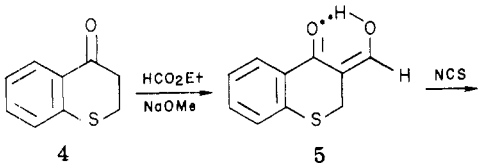


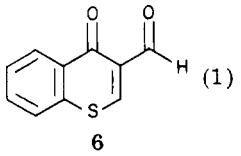
2

Existing methodology for functionalizing C-3 of thiopyrans is not well documented.[2] Recently, it was reported[3] that certain 3-formyl-2*H*-dihydrothiopyrans **2** can be prepared from 3-mercapto aldehydes and α,β-unsaturated carbonyl compounds by a conjugate addition–aldol condensation reaction. This route, however, could not be applied to the synthesis of phenyl-substituted derivatives of **2**, presumably owing to the lability of the benzylic mercapto group under the reaction conditions. We describe here our syntheses of **1** and related compounds.

On the basis of some of our earlier work dealing with the synthesis of 4*H*-thiopyran-4-ones,[4] we sought to synthesize **1** from the corresponding tetrahydro derivative **3**. In a model study, we prepared 3-formyl-4*H*-thiochroman-4-one (**5**) from the enolate of 4*H*-thiochroman-

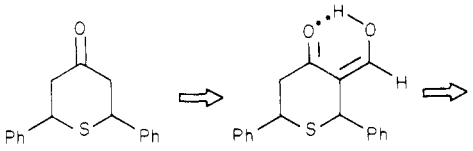


4 **5**

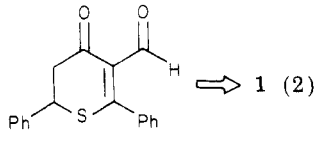


6 (1)

4-one (**4**) using ethyl formate and sodium methoxide.[5] Treatment of **5** under oxidative elimination conditions, using *N*-chlorosuccinimide (NCS) with or without pyridine, gave the desired dehydrogenated 3-formyl-4*H*-thiochromone (**6**) (eq 1) in essentially quantitative yield. This result suggested that **3** would be a suitable intermediate for the preparation of **1** by the route shown in eq 2.



7 **3**



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Although the parent 3-formyl-4*H*-tetrahydrothiopyran-4-one[6] has been prepared from the corresponding 4*H*-tetrahydrothiopyran-4-one in the same manner as **5**, the synthesis of **3** was hitherto unknown. Numerous attempts were directed toward the synthesis of **3** from the corresponding 2,6-diphenyl-4*H*-tetrahydrothiopyran-4-one (**7**),[7] such as the formylation of the corresponding enamines (pyrrolidine or morpholine)[8] and the enolate using the standard procedures.[5,6] None of these methods, however, were fruitful. Treating **7** with the dimethyl acetal of DMF, we isolated 3-[(dimethylamino)methylene]-2,6-diphenyl-4*H*-tetrahydrothiopyran-4-one (**13**) in 24% yield. Acetolysis of **13** in the presence of a small amount of dilute sulfuric acid successfully removed the dimethylamine function to give the desired **3**. Subsequent dehydrogenation of **3** in attempts to prepare the 5,6-dihydro compound **8** (eq 2) using selenium dioxide or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was, however, unsuccessful. Other approaches were then undertaken.

Treatment of **7** under Vilsmeier conditions[9,10] gave a mixture of products from which the β-chlorovinyl aldehyde **9** was isolated in 40% crude yield. Under similar conditions, 2,6-diphenyl-4*H*-dihydro-thiopyran-4-one (**10**)[4] gave a mixture of two products which were separated by high-pressure liquid chromatography over silica gel to give 30% of 4-chloro-2,6-diphenyl-3-formyl-2*H*-thiopyran (**11**), 37% of an unstable dark oil to which was assigned the structure of 4-chloro-2,6-diphenyl-2*H*-thiopyran (**12**) on the basis of the NMR and mass spectroscopic data, and

(1) J. H. Perlstein, *Angew. Chem., Int. Ed. Engl.* **16**, 519 (1977).
(2) For a brief review on thiopyrans, see V. G. Kharchenko, S. N. Chalaya, and T. M. Konovalova, *Kim. Geterotsikl. Soedin.*, 1003 (1976).
(3) J. M. McIntosh and H. Khalil, *J. Org. Chem.*, **42**, 2123 (1977).
(4) C. H. Chen, G. A. Reynolds, and J. A. Van Allan, *J. Org. Chem.*, **42**, 2777 (1977); C. H. Chen, *Heterocycles*, **7**, 231 (1977).
(5) V. N. Gogte, K. A. R. Sastry, and B. D. Tilak, *Indian J. Chem.*, **12**, 1147 (1974).
(6) P. Schenone, L. Mosti, and G. Bignardi, *J. Heterocycl. Chem.*, **13**, 225 (1976).
(7) F. Arndt, P. Nachtweg, and J. Pusch, *Chem. Ber.*, **58**, 1633 (1925).
(8) W. Ziegenbein, *Angew. Chem.*, **77**, 380 (1965); Z. Arnold, *Experientia*, **15**, 415 (1959).
(9) For review, see M. Pulst and M. Weissenfels, *Z. Chem.*, **16**, 337 (1976).
(10) A. Rocci, D. Balucani, A. Fravolini, F. Schiaffella, and G. Grandolini, *Gazz. Chim. Ital.*, **107**, 19 (1977).

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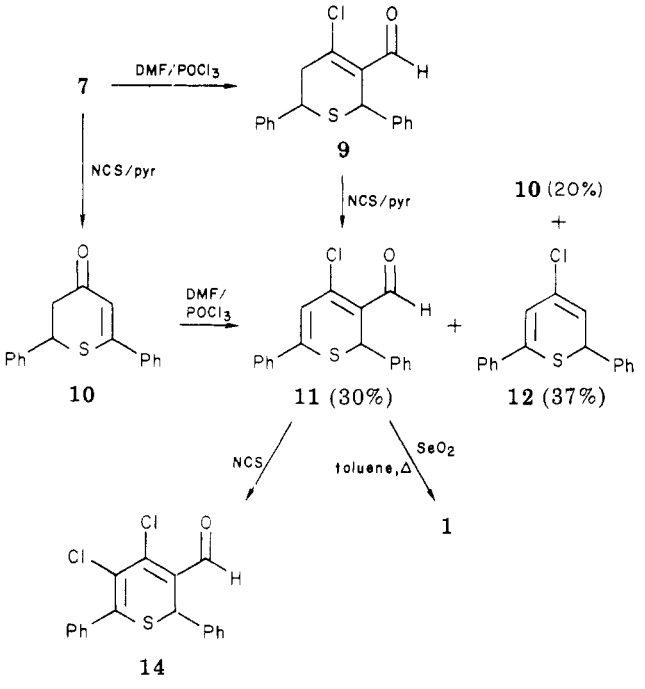
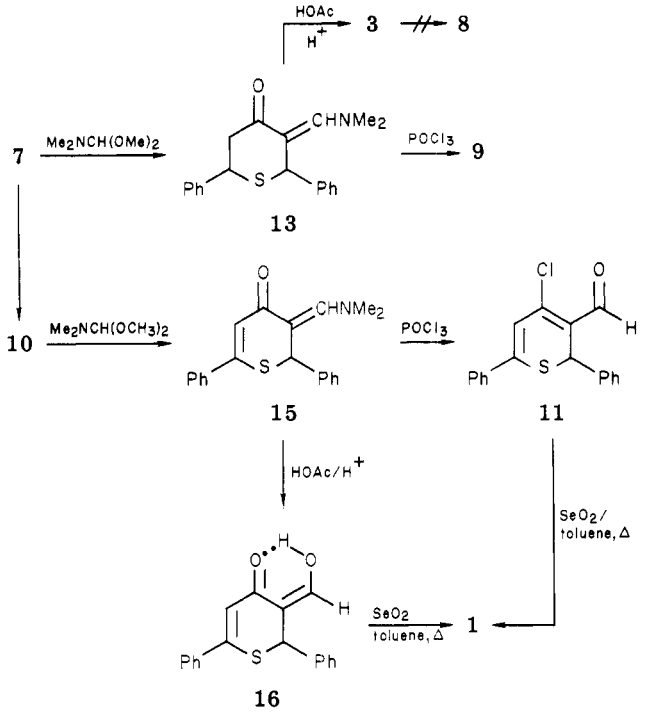
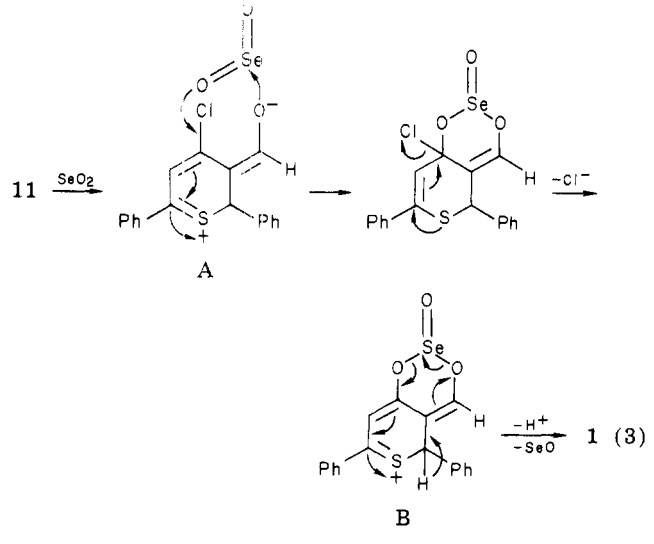
Scheme I



Scheme II

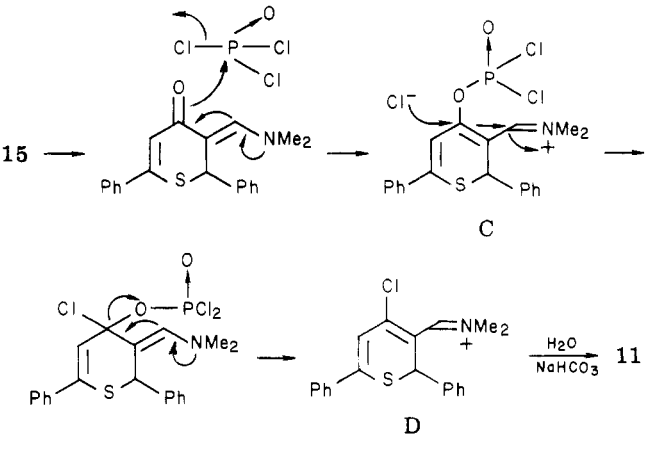


20% of recovered starting material (Scheme I). Treating **11**, which can also be prepared from **9** by oxidative elimination using NCS and pyridine,[4] with 1 equiv of NCS, we obtained a chloro-substituted compound to which we assigned structure **14** in accord with its NMR and mass spectra. Presumably this compound is formed as the result of the electrophilic substitution of the vinylic sulfide moiety of **11**.[2] Selenium dioxide oxidation of **11** in refluxing toluene gave **1** in 82% yield. This somewhat surprising result suggested that the vinyl sulfide chromophore which is conjugated with the β-chlorovinyl aldehyde group in **11** causes the carbonyl oxygen to be nucleophilic toward selenium dioxide. Although the detailed mechanism of selenium dioxide oxidations is uncertain,[11] a likely mechanism in this system may involve an intramolecular addition–elimination via a six-membered transition state A which leads eventually to the intermediate B (eq 3). Deprotonation of the very acidic



benzylic proton in B should give **1** with concurrent reduction of Se^{4+} to the unstable selenium monoxide[12,13] which, under the reaction conditions (acidic), disproportionates into selenium and the dioxide.[13,14] Additional evidence for the proposed mechanism was provided by the fact that hydrogen chloride was detected from this reaction, and contrary to the normal selenium dioxide dehydrogenation,[11] **1** was formed directly without the formation of water. The solid which precipitated from the reaction in toluene was grayish and mostly water soluble, and only very little selenium was isolated. Furthermore, *the dihydro-β-chlorovinyl aldehyde* ***9****, which does not contain the vinyl sulfide linkage, was totally unreactive*

Scheme III



(11) R. A. Jurussi in "Selective Organic Transformation", Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, 1970, pp 301–26.

(12) V. Lenher, *J. Am. Chem. Soc.*, **20**, 555 (1898); R. K. Asundi, M. Jan-Khan, and R. Samuel, *Proc. R. Soc. London, Ser. A.*, **157**, 28(1936).

(13) Although the properties of SeO are unknown owing to its extreme lability, a related compound, $SeSO_3$, has been reported to decompose into Se, SeO_2, and SO_2 on heating [G. Lucovsky, "The Physics of Selenium and Tellurium", W. Charles Cooper, Ed., Pergamon Press, Oxford, 1969, p 255].

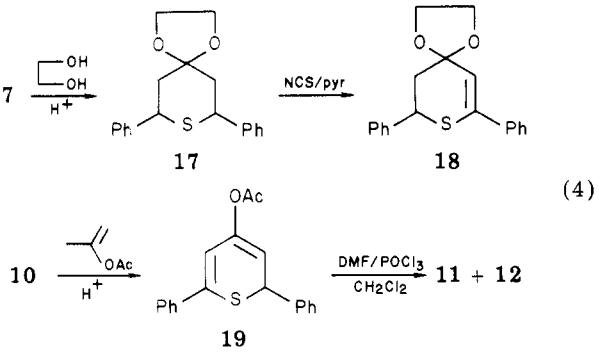
(14) The properties of the closely related sulfur monoxide are well documented [P. W. Schenk and R. Steudel, *Angew. Chem., Int. Ed. Engl.*, 4, 402 (1965)]. Sulfur monoxide is a true biradical which is extremely reactive and thermodynamically unstable, decomposing spontaneously into sulfur and SO_2 according to $2SO \rightarrow S_{rhomb} + SO_2$ ($\Delta H_0^0 = -36.8$ kcal/mol).

toward selenium dioxide under the same conditions.

In attempts to eliminate the major chlorinated by-product **12** which is obtained under the Vilsmeier conditions (Scheme I), we found that the dimethyl acetal of DMF is the reagent of choice. Thus, yellow crystalline 3-[(dimethylamino)methylene]-2,6-diphenyl-4*H*-dihydrothiopyran-4-one (**15**), which was obtained in 69% yield from **10** (Scheme II), was readily deaminated in the presence of phosphoryl chloride to give **11** (77%). Presumably, in the presence of $POCl_3$, **15** was converted to C which underwent addition–elimination (Scheme III) to give the iminium ion D from which **11** was obtained on hydrolysis. Similarly, the dihydro-β-chlorovinyl aldehyde **9** can also be obtained from the corresponding 3-(dimethylamino)methylene derivative **13**.

Aqueous sodium acetate did not hydrolyze the dimethylamino function in **15**, and aqueous sodium hydroxide gave **10**, but acetolysis in the presence of a catalytic amount of dilute sulfuric acid smoothly transformed **15** to the desired β-keto aldehyde **16** (Scheme II). Selenium dioxide dehydrogenation of **16** in the usual manner[11] gave **1** in high yield. The mechanism of this selenium dioxide oxidation in which water and selenium are generated must be of the normal type[11] that is different from that proposed for **11** (eq 3).

Certain derivatives of **7** with a masked ketone function were also prepared (eq 4). The ketal **18**, on treatment with



(4)

the Vilsmeier reagent ($DMF/POCl_3$), gave a complex mixture of products.[15] Under the same conditions, the enol acetate **19** gave mostly **12** (about 80% as estimated by the NMR of the reaction mixture) and a small amount of **11**. This approach was not pursued further.

Experimental Section

Melting points (uncorrected) were obtained on a Mettler FPI instrument. NMR spectra were recorded on a Varian T-60 spectrometer using $CDCl_3$ as solvent and tetramethylsilane as an internal standard. Mass spectra were obtained on a Hitachi RMS-4 mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer. Liquid chromatography was done on a Waters Associates preparative LC/system 500 unit. Thin-layer chromatography was done on silica gel plates 0.25 mm thick. Elemental analyses were done by the Analytical Sciences Division, Kodak Research Laboratories.

3-Formyl-4*H*-thiochromone (6). To a cooled (ice) solution of 10.8 g (0.056 mol) of 3-formyl-4*H*-thiochroman-4-one (**5**)[5] was added 7.8 g (0.058 mol) of *N*-chlorosuccinimide slowly (10 min). The solution gradually turned from light brown to colorless and was stirred at ambient temperature for 2 h (HCl was detected from the reaction). The solvent was removed on a Rotavap, and the solid residue was washed with water and air-dried to give 10.7 g (100%) of an essentially pure product: ^1H NMR δ 7.6 (m, 4 H, aromatic), 8.6 (m, 1 H), 10.3 (s, 1 H, aldehyde); IR (KBr) 1625, 1680 cm^{-1} (C=O). An analytical sample was obtained by recrystallization from toluene and hexanes, mp 152.2 °C. Anal. Calcd for $C_{10}H_6O_2S$ (mol wt 190): C, 63.1; H, 3.2; S, 16.9. Found: C, 63.1; H, 3.6; S, 16.8.

4-Chloro-2,6-diphenyl-3-formyl-2*H*-dihydrothiopyran (9). Method I. A solution of 10 g (0.0373 mol) of diastereoisomeric 2,6-diphenyl-4*H*-tetrahydrothiopyran-4-one (**7**)[4] in methylene chloride was added dropwise to the Vilsmeier reagent prepared by adding dropwise a solution of 5.73 g of phosphoryl chloride in 10 mL of methylene chloride to a solution of 4 g of DMF in 20 mL of methylene chloride at ambient temperature.[16] The resulting reddish solution was kept at room temperature overnight and then poured into 150 mL of aqueous sodium acetate. The organic layer was separated, dried ($MgSO_4$), concentrated on a Rotavap, and purified by short-path vacuum distillation to give 4.7 g (40%) of a crude product [bp 108–114 °C (2–3 μmHg)] in the form of a yellow viscous oil which slowly solidified on standing. Further purification by column chromatography over silica gel (eluted with methylene chloride) gave about 1 g of an analytically pure sample: mp 111.9 °C (hexanes); NMR δ 3.2 (d, 2 H), 3.9 (t, 1 H), 5 (s, 1 H), 7.1 (m, 10 H, aromatic), 10.3 (s, 1 H, –CHO); IR (KBr) 1680 cm^{-1} (C=O); mass spectrum, *m/e* 314 (M^+). Anal. Calcd for $C_{18}H_{15}ClOS$ (mol wt 314): C, 68.7; H, 4.8; Cl, 11.3. Found: C, 68.9; H, 4.7; Cl, 11.4.

Method II. A mixture of 6 g (0.0225 mol) of **7**, 6 mL of the dimethyl acetal of dimethylformamide, and 50 mL of toluene was heated in a round-bottom flask equipped with a still head, and the methyl alcohol that formed was distilled. When no more alcohol came over (about 6 h), the reaction mixture was cooled, diluted with petroleum ether, and allowed to stand overnight. The solid was collected and recrystallized from toluene, yielding 1.8 g (24%) of 5-[(dimethylamino)methylene]-2,3-dihydro-4*H*-thiopyran-4-one (**13**), mp 172–173 °C. Anal. Calcd for $C_{20}H_{21}NOS$ (mol wt 323): C, 74.3; H, 6.5; N, 4.3. Found: C, 74.7, H, 6.2; N, 4.5.

To a solution of 3.7 g (0.0117 mol) of **13** in 50 mL of methylene chloride was added 1 mL of phosphoryl chloride; the mixture was stirred for 2 h, made basic with aqueous sodium bicarbonate, and stirred for 2 h more. The organic phase was separated and the solvent removed. The residue was recrystallized from isopropyl alcohol, yielding 2 g (63%) of **9**, mp 112 °C. The IR and NMR spectra were identical with those of the product obtained by method I.

2,6-Diphenyl-3-formyl-4*H*-tetrahydrothiopyran-4-one (3). To a solution of 1.6 g (49 mmol) of **13** in 10 mL of glacial acetic acid was added 20 drops of 10% sulfuric acid. Following stirring at ambient temperature overnight, the mixture was poured onto ice, extracted with methylene chloride, and washed with sodium bicarbonate followed by water. The organic extract was dried ($MgSO_4$) and concentrated to give 1.4 g (96%) of pure **3** in the form of a light brown oil: NMR δ 3.0 (d, J = 8 Hz, 2 H, methylene), 3.97 (t, J = 8 Hz, 1 H, C-6 benzylic), 4.82 (s, 1 H, C-2 benzylic), 7–7.2 (m, 11 H, aromatic and enolic vinyl), 8.40 (s, 1 H, enol); mass spectrum, *m/e* 296.0886 (calcd M^+ for $C_{18}H_{16}O_2S$, 296.0870). Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.9; H, 5.4; S, 10.8. Found: C, 72.6; H, 5.8; S, 10.5.

4-Chloro-2,6-diphenyl-3-formyl-2*H*-thiopyran (11). Method I. A solution of 13.3 g (0.05 mol) of 2.6-diphenyl-4*H*-2,3-dihydrothiopyran-4-one (**10**) in 25 mL of methylene chloride was added to the Vilsmeier reagent prepared from 5 mL of DMF and 5.7 mL of phosphoryl chloride in methylene chloride.[16] The reaction mixture was heated on a steam bath and the methylene chloride allowed to evaporate. The residue was heated an additional 2 h and cooled to room temperature, and excess aqueous sodium acetate was added. The mixture was diluted with 100 mL of methylene chloride and stirred overnight. The methylene chloride layer was separated, washed with water, dried ($MgSO_4$), and concentrated to 25 mL. The mixture of products was separated by high-pressure liquid chromatography on silica gel, eluting with methylene chloride to give 4.7 g (30%) of **11**, 5.2 g (37%) of 4-chloro-2,6-diphenyl-2*H*-thiopyran (**12**), and 2.65 g (20%) of recovered starting material (**10**).

(15) Ethylene ketals were reported to react with the Vilsmeier reagent to give ring-opened products [D. Burn, G. Cooley, M. T. Davies, J. W. Ducker, B. Ellis, P. Feather, A. K. Hiscock, D. N. Kirk, A. P. Leftwick, V. Petrow, and D. M. Williamson, *Tetrahedron*, **20**, 597 (1964)].

(16) L. A. Paquette, B. A. Johnson, and F. M. Hinga, "Organic Syntheses", Collect. Vol. V, Wiley, New York, 1973, p 215.

An analytical sample of **11** was obtained by recrystallization from hexanes: mp 95.1 °C; NMR δ 5.4 (s, 1 H, benzylic), 6.55 (s, 1 H, C-5 vinylic), 7–7.6 (m, 10 H, aromatic), 10.3 (s, 1 H, aldehyde); IR (KBr) 1655 cm^{-1} (C=O); mass spectrum, *m/e* 312 (M^+ for $C_{18}H_{13}{}^{35}ClOS$), 283 (M^+ – CHO). Anal. Calcd for $C_{18}H_{13}ClOS$ (mol wt 312.5): C, 69.1; H, 4.2; S, 10.3; Cl, 11.3. Found: C, 69.5; H, 4.6; S, 10.7; Cl, 11.0.

Owing to the labile nature of **12** (turned dark on keeping), an analytical sample was not obtained. The structure of **12** was supported by its NMR and mass spectra: NMR δ 4.9 (d, J = 6 Hz, 1 H, benzylic), 5.77 (dd, J = 6 and 1 Hz, 1 H, C-5 vinylic), 6.4 (d, J = 1 Hz, 1 H, C-3 vinylic), 7.3 (m, 10 H, aromatic); mass spectrum, *m/e* 284 (M^+ for $C_{17}H_{13}{}^{35}ClS$).

Method II. A mixture of 6 g (0.0225 mol) of **10**, 5 mL of the dimethyl acetal of dimethylformamide, and 50 mL of toluene was heated, and the methyl alcohol that was formed was distilled from the reaction mixture. When no more alcohol was formed, the solution was chilled, and the solid was collected and recrystallized from toluene to give 5 g (69%) of **15**, mp 193 °C. Anal. Calcd for $C_{20}H_{19}NOS$ (mol wt 321): C, 74.7; H, 6.0; N, 4.4. Found: C, 74.6; H, 6.1; N, 4.5.

A solution of 5 g (0.0156 mol) of **15**, 1.5 mL of phosphoryl chloride, and 100 mL of methylene chloride was stirred for 2 h, made basic with aqueous sodium bicarbonate, and stirred for 2 h more. The organic layer was separated, the solvent was evaporated, and the residue was recrystallized from hexanes to yield 3.7 g (81%) of **11**, mp 90 °C. The IR was identical with that of the product obtained by method I.

4,5-Dichloro-2,6-diphenyl-3-formyl-2*H*-thiopyran (14). To a solution of 147 mg (0.5 mmol) of **11** in 1 mL of deuteriochloroform was added 70 mg of *N*-chlorosuccinimide (NCS) at room temperature in an NMR tube. The reaction was followed by the gradual disappearance from the NMR spectra of a singlet at δ 2.85 and the formation of a new singlet at δ 2.7 which is due to the succinimide. The solution was poured into water and extracted with methylene chloride, and the extract was subjected to preparative TLC on silica gel (20 cm × 20 cm × 2 mm) to give 80 mg of a yellow oil. The NMR [δ 5.34 (s, 1 H, benzylic), 7.3 (m, 10 H, aromatic), 10.3 (s, 1 H, aldehyde)] and mass spectra [*m/e* 346 ($(^{35}Cl_2)$ M^+), 317 ($(^{35}Cl_2)$ (M^+ – CHO), 283 ($(^{35}Cl_1)$, 281 ($(^{35}Cl_1)$, 247] agreed with structure **14**.

2,6-Diphenyl-3-formyl-4*H*-thiopyran-4-one (1) from 11. A mixture of 1 g (3.2 mmol) of **11** and 450 mg (4 mmol) of selenium dioxide in 25 mL of toluene was refluxed for 14 h. The light gray solid was removed by filtration, and the clear filtrate was concentrated on a Rotavap to give about 1 g of a yellow solid which was recrystallized from benzene and hexanes to give 750 mg (82%) of pure **1**: mp 124–125 °C; NMR δ 7.22 (s, 1 H, vinylic), 7.4 (m, 10 H, aromatic), 10.2 (s, 1 H, –CHO); IR (KBr) 1620, 1700 cm^{-1} (C=O); mass spectrum, *m/e* 292 (M^+). Anal. Calcd for $C_{18}H_{12}O_2S$ (mol wt 292): C, 74.0; H, 4.1; S, 11.0 Found: C, 73.6; H, 4.2; S, 10.8. The reaction was repeated on a 1-mmol scale, and the gray solid was added to water and the solution filtered to give 8 mg of selenium metal.

2,6-Diphenyl-3-formyl-4*H*-dihydrothiopyran-4-one (16). A solution of 3 g (0.01 mol) of **15** in 25 mL of glacial acetic acid containing a few drops of 10% H_2SO_4 was stirred at ambient temperature. The reaction was followed by TLC (silica gel). After completion (about 24 h) of the reaction, the solution was poured into 500 mL of brine from which a reddish brown gum precipitated. After brief cooling to allow the gummy product to solidify, the mixture was filtered and the solid washed thoroughly with water. The crude product, 2.6 g (95%), which was suitable for further reaction, was recrystallized from a small amount of hexanes to give pure **16**: mp 84.5 °C; NMR δ 5.03 (br s, 1 H, benzylic), 6.42 (s, 1 H, vinylic), 7.0–7.7 (m, 11 H), 8.1 (s, 1 H); IR (KBr) 1620 (br) cm^{-1} (C=O); mass spectrum, *m/e* 294 (M^+), 265 (M^+ – CHO). Anal. Calcd for $C_{18}H_{14}O_2S$ (mol wt 294): C, 73.4; H, 4.8; S, 10.9. Found: C, 73.8, H, 4.8; S, 10.8.

2,6-Diphenyl-3-formyl-4*H*-thiopyran-4-one (1) from 16. A mixture of 2.6 g (8.8 mmol) of crude **16** from the previous reaction, 1.24 g (1.2 equiv) of selenium dioxide, and 200 mL of toluene was refluxed for 16 h while the water was removed by a Dean–Stark trap. The deposited selenium metal was removed by filtration over Celite, and the reddish brown clear filtrate was concentrated on a Rotavap. The solid thus obtained was recrystallized from toluene and hexanes to give 2.3 g (84% based on **15**) of **1**, whose structure was confirmed by comparison with an authentic sample. A second crop of about 80 mg was obtained by concentrating the mother liquor.

4-Chloro-2,6-diphenyl-3-formyl-2*H*-thiopyran (11) from 9. To a solution of 380 mg (1.22 mmol) of **9** and 175 mg of pyridine in 15 mL of methylene chloride was added 280 mg of NCS. The solution, kept at ambient temperature for 2 days, was washed with water, dried ($MgSO_4$), and concentrated on a Rotavap to give 400 mg of a crude product which was purified by preparative TLC (silica gel, 2 mm thick, eluted wih toluene–hexanes), giving 250 mg (66%) of pure **11**. This material was identical in every respect with an authentic sample prepared from **10** (vide supra).

4-Acetoxy-2,6-diphenyl-2*H*-thiopyran (19). A solution of 10 g (0.037 mol) of **10** and 400 mg of *p*-toluenesulfonic acid in 20 mL of isopropenyl acetate was azeotropically distilled by using a Dean–Stark trap over 4 h. The mixture was concentrated, poured into aqueous $NaHCO_3$, and extracted with ether. The ether extracts were combined, washed with H_2O, dried ($MgSO_4$), and concentrated on a Rotavap, and the residue was vacuum distilled to give 9.2 g (84%) of **19**: bp 116 °C (2 μmHg); NMR δ 2.28 (s, 3 H, CH_3), 5.1 (d, J = 6 Hz, 1 H, benzylic), 5.62 (dd, J = 6 and 1 Hz, 1 H, C-3 vinylic proton), 6.38 (d, J = 1 Hz, 1 H, C-5 vinylic), 7.3–8.0 (m, 10 H, aromatic). Anal. Calcd for $C_{19}H_{16}O_2S$: C, 74.0; H, 5.2; S, 10.4. Found: C, 74.4; H, 5.5; S, 10.1.

2,6-Diphenyl-4*H*-tetrohydrothiopyran-4-one Ethylene Ketal (17). A mixture of 10 g (0.0374 mol) of diastereoisomeric **7**, 2.4 g of ethylene glycol, 500 mg of *p*-toluenesulfonic acid, and 200 mL of benzene was azeotroped for 8 h. The mixture was washed with aqueous sodium bicarbonate and with water, and the benzene solution was dried ($MgSO_4$). The solution was concentrated in vacuo to give 11.6 g of a solid which was recrystallized from 300 mL of hexanes, giving 9.4 g (81%) of pure **17**: mp 130.1 °C; NMR δ 2.16 (br d, 4 H, methylene), 3.88 (s, 4 H, ethylene ketal), 4.2 (t, 2 H, benzylic), 7.0–7.5 (m, 10 H, aromatic). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.1; H, 6.5; S, 10.3. Found: C, 73.1; H, 6.6; S, 10.5. A second crop of 1.6 g was obtained on concentration of the mother liquor and recrystallization from 20 mL of methanol.

2,6-Diphenyl-4*H*-dihydrothiopyran-4-one Ethylene Ketal (18). To a solution of 1 g (3.2 mmol) of **17** and 279 mg of pyridine in 10 mL of methylene chloride was added 450 mg of NCS. The solution was kept at ambient temperature overnight, washed with water, dried ($MgSO_4$), and concentrated on a Rotavap to give a colorless oil which was purified by preparative TLC (silica gel/methylene chloride) to give 850 mg (86%) of **18**: NMR δ 2.3 (m, 2 H), 3.95 (m, 4 H), 4.5 (m, 1 H, benzylic), 5.75 (s, 1 H, vinylic), 7.2 (m, 10 H, aromatic); mass spectrum, *m/e* 310 (M^+). Anal. Calcd for $C_{19}H_{18}O_2S$: C, 73.5; H, 5.8; S, 10.3. Found: C, 73.1; H, 5.7; S, 10.3.

Registry No. **1**, 70940-96-4; *cis*-**3**, 70940-97-5; *trans*-**3**, 70940-98-6; **5**, 6125-45-7; **6**, 70940-99-7; *cis*-**7**, 18456-44-5; *trans*-**7**, 37014-01-0; *cis*-**9**, 70941-00-3; *trans*-**9**, 70941-01-4; **10**, 60839-95-4; **11**, 70941-02-5; **12**, 70941-03-6; *cis*-**13**, 70941-04-7; *trans*-**13**, 70941-05-8; **14**, 70941-06-9; **15**, 70982-63-7; **16**, 70941-07-0; *cis*-**17**, 70941-08-1; *trans*-**17**, 70941-09-2; **18**, 70941-10-5; **19**, 70941-11-6; dimethylformamide dimethyl acetal, 4637-24-5.