Table I. X-ray Analysis of 12, $C_{32}H_{24}OS_2$

parameter	
cell dimensions	
a, Å	10.381 (3)
b, Å	15.004 (3)
c, Å	9.433 (3)
α, deg	109.67 (2)
β, deg	112.82 (2)
γ, deg	79.56 (2)
V, Å^3	1273.1 (13)
Z (molecules per unit cell)	2
D_c, g cm^{-3}	1.275
μ (Mo Kα), cm^{-1}	2.30
λ, Å	0.7107
unique reflections	3305
scan range, deg	2θ(Mo Kα_1) −0.6° to 2θ(Mo Kα_2) + 0.6°
scan rate, 2θ/min	1.8–20°
range of data	0° < 2θ(Mo Kα) < 45°

for all atoms, were obtained from International Tables for X-ray Crystallography, Vol. IV, 1974. Refinement proceeded smoothly and converted to $R = \sum ||F_o| - K|F_c|| / \sum |F_o| = 0.077$ and $R_w = (\sum w (|F_o - K|F_c|)^2 / \sum wF_o^2)^{1/2} = 0.085$ for the 35 non-hydrogen atoms with anisotropic temperature factors. A total of 316 parameters were varied and 2045 reflections were used. The estimated standard deviation of an observation of unit weight was 2.47. A final different electron density map showed a maximum density of 0.44 e/Å^3. In a final electron density map, the peak electron densities of the atoms were relatively low—only 19.0 and 15.4 e/Å^3 for S1 and S2 down to a low of 2.6 e/Å^3 for C26.

Acknowledgment. We are indebted to L. W. Kelts and S. M. Finn for recording many of the Supercon-NMR spectra and to F. D. Saeva for obtaining the cyclic voltammogram.

Registry No. 4, 93383-45-0; 5, 51317-73-8; 7, 70660-17-2; 8, 93383-33-6; 11, 70940-96-4; (*Z*)-12, 93383-34-7; 13, 93383-36-9; 14, 93383-37-0; (*Z*)-15, 93383-38-1; (*Z*)-16, 93383-39-2; 18, 93383-41-6; 20, 93383-42-7; 21, 93383-40-5; 22, 93383-43-8; 23, 93383-44-9; $(PhCH_2)_2S$, 538-74-9; $P(OEt)_3$, 122-52-1.

Supplementary Material Available: Atomic parameters (Table II), generalized anisotropic thermal parameters (Table III), bond lengths (Table IV), and bond angles (Table V) for compound 12 (4 pages). Ordering information is given on any current masthead page.

Thiopyranothiopyran Chemistry. 2. Synthesis of 2,4-Diphenyl-4*H*-benzo[*e*]thiopyrano[3,4-*b*]thiopyran-10-one†

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Received March 12, 1984

2,4-Diphenyl-4*H*-benzo[*e*]thiopyrano[3,4-*b*]thiopyran-10-one was synthesized by lithiation of 3-[2(*Z*)-(benzylsulfinyl)-2-phenylethenyl]-4*H*-thiochroman-4-one, whose absolute configuration was established by X-ray crystallography. The yellow, insoluble solid obtained from this reaction was assigned the structure 2,6-diphenyl-2*H*-4-(2-mercaptobenzoyl)thiopyran 1-oxide (11), which, on brief heating with AcOH, yielded the title compound in 87% yield. Treatment of 11 with 1% aqueous cupric acetate in methylene chloride gave a new rearranged product, which was identified as 9,11-diphenylbenzo[*b*]-1,8-dithiaspiro-[4,5]deca-6,9-dien-4-one. Mechanisms that would account for the formation of both of these compounds are proposed.

In the first part of this series,[1] we described the synthesis of the novel dihydrothiopyrano[3,4-*b*]thiopyranyl sulfone derivative **2**, which we believe to be derived from an addition–elimination reaction of the lithiated anion A at C-2 of (*Z*)-1 followed by an intramolecular Michael addition of C, as depicted in Scheme I. The yield of **2**, however, was only 10%, and most of the starting material 1 was recovered. We attributed the low yield of this reaction to the phenyl substituent at C-2, which was somewhat hindered to nucleophilic attack. Thus, we reasoned that a compound without the C-2 substituent should readily undergo the initial Michael addition to give an enolate intermediate similar to B. Since this Michael adduct already embodies the desired thiopyrano[3,4-*b*]thiopyranyl framework, it might be trapped under favorable conditions without further rearrangement. This paper describes the synthesis and the stereochemistry of the thiochroman derivative **6** and its cyclization to give the desired thiopyrano[3,4-*b*]thiopyran **12**.

Results and Discussion

Synthesis of 3-[2(*Z*)-(Benzylthio)-2-phenylethenyl]-4*H*-thiochroman-4-one (5) and Derivatives. **Single-Crystal X-ray Diffraction Analysis of the Sulfone 8.** 3-Formyl-4*H*-thiochroman-4-one (**3**),[2] readily prepared from thiochroman-4-one, was condensed with the Wittig–Horner reagent of diethyl α-(benzylthio)benzylphosphonate (**4**)[1] in THF at −78 °C to give **5** in 81% yield as a single isomer. The high stereospecificity of this reaction, though not totally unexpected,[1] is quite remarkable. Since only the *Z* isomer can ring close to the desired [3,4-*b*] system, it is crucial, at this stage of the synthesis, that the stereochemistry of **5** be confirmed. Various NMR techniques involving NOE and shift reagents were attempted, but, unfortunately, they failed to yield enough information to allow us to assign the stereoconfiguration of **5**.

Oxidation of **5** with 1 and 2 equiv of *m*-chloroperbenzoic acid (MCPBA) in methylene chloride gave the sulfoxide **6** and the sulfone **8**, respectively, in high yields. Since single crystals suitable for X-ray diffraction analysis were difficult to prepare from either the sulfide **5** or the sulfoxide **6**, crystallographic analysis was performed on a single crystal of the sulfone **8**, which was obtained by slow recrystallization from acetonitrile at room temperature. A stereodrawing of **8** with atomic labeling and bond lengths,

† Dedicated to Dr. George A. Reynolds on the occasion of his retirement from the Kodak Research Laboratories.

(1) Chen, C. H.; Reynolds, G. A.; Smith, D. L.; Fox, J. L. *J. Org. Chem.*, preceding paper in this issue.
(2) Chen, C. H.; Reynolds, G. A. *J. Org. Chem.* **1979**, *44*, 3144.

0022-3263/84/1949-5143$01.50/0

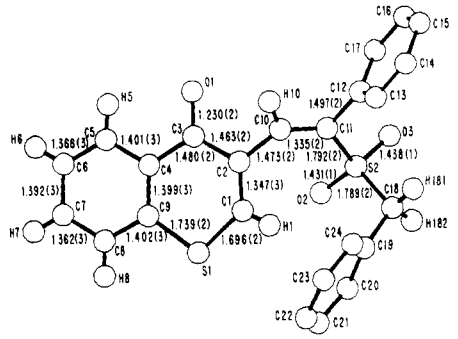
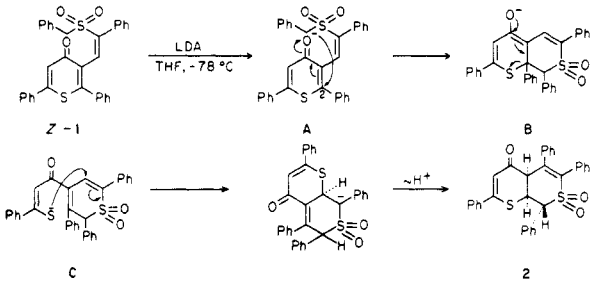


Figure 1. Stereodrawing of 8 with atomic labeling and selected bond lengths. Estimated standard deviations are given in parentheses. Phenyl hydrogens are omitted for clarity.

Scheme I



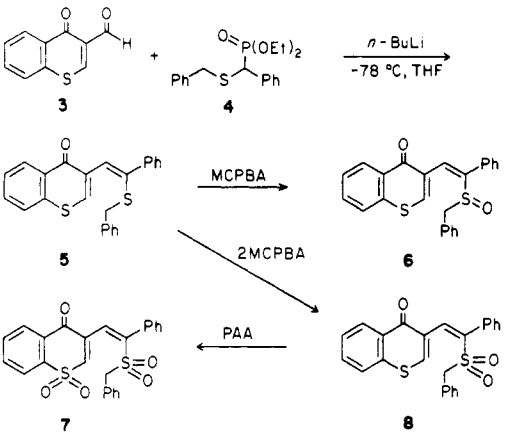
which provided the unequivocal assignment of the *Z* stereoconfiguration about the C10=C11 double bond, is shown in Figure 1 (bond angles are omitted for clarity). Bond lengths in the thiochroman ring system deviate slightly from the expected values. In particular, there is considerable localization of the double bonds at C5=C6 and C7=C8, whereas S1—C9 and C3—C4 are nearly normal single bonds. There is some double-bond character to S1—C1 (1.696 ± 2 Å) and C2—C3 (1.463 ± 2 Å), indicating a significant contribution of the resonance form involving the delocalization of the lone pair on sulfur into the carbonyl.

This delocalization is also reflected in the IR spectrum of **8**, which has a carbonyl band at 1620 cm^{-1} that is considerably lower than those of normal α,β-unsaturated ketones. We were delighted to find the distance between the benzylic carbon (C-18) and C-1 is only about 4.13 Å, which is favorable for the anticipated nucleophilic annulation.

Because the conditions for MCPBA oxidations are so mild,[3] we have no reason to suspect that the configurations of **5** and **6** would be different from that of (*Z*)-**8** owing to isomerization. The preferred conformations of **5**, **6**, and **8** in solution appear to be similar to that of **8** in the solid state, with the benzyl group near C-2 of the thiochroman ring, as depicted in Scheme II. This rationalization is supported by the lack of temperature dependence of the benzylic protons of these compounds detected in the NMR probe from −60 to +150 °C. These conformations are quite different from those of compounds bearing a C-2 phenyl substituent (such as (*Z*)-**1**), in which the benzyl group prefers to be near the carbonyl group.[1]

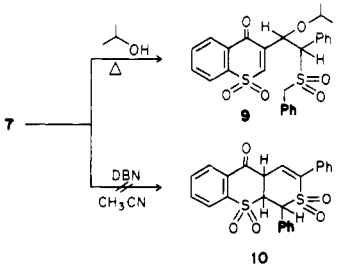
Since the outcome of the subsequent nucleophilic cyclizations to give either the [4,3-*c*]- or the [3,4-*b*]thiopyranothiopyranyl system depends largely on the preferred conformations of the starting materials in solution, it is gratifying to note that the desired conformations have been achieved, for the most part, by removing the substituent at C-2. Further oxidation of **8** with 40% peracetic acid

Scheme II



(PAA) at 40–45 °C gave the disulfone **7**, which could also be obtained directly from **5** by exhaustive oxidation with excess PAA. The shift of the IR carbonyl stretching frequency from 1620 (**8**) to 1675 cm^{-1} (**7**) is indicative of the disruption of the delocalization associated with the lone pair on sulfur of the thiochroman-4-one system.

Attempted Cyclizations of 5, 8, and 7. Attempted cyclization of the sulfide **5** with LDA or lithio-2,2,6,6-tetramethylpiperidine[4] in THF failed to produce either the [3,4-*b*]- or the [4,3-*c*]thiopyranothiopyranyl system under a variety of experimental conditions. In light of the failures experienced during the cyclization of 3-[2(*Z*)-(benzylthio)-2-phenylethenyl]-2,6-diphenyl-4*H*-thiopyran-4-one in part 1 of this research,[1] these results, although disappointing, were not unexpected. The failure of the monosulfone **8** to cyclize at C-2 under a variety of irreversible and reversible basic conditions ranging from LDA/THF/−78 °C to sodium *tert*-amylate/toluene and 1,5-diazabicyclo[4,3]non-5-ene (DBN)/acetonitrile was surprising. Presumably, the anion of **8** was not nucleophilic enough to Michael-add to the C-2 position, which was rendered somewhat less electrophilic by the adjacent lone pair on sulfur. We then focused our attention on the cyclization of the disulfone **7**, which also turned out to be a formidable task. For instance, we soon found that the vinylic sulfone portion of **7** was extremely susceptible to Michael addition even in the presence of as mild a nucleophile as isopropyl alcohol! Thus, merely recrystallizing crude **7** from isopropyl alcohol gave a small amount of the adduct **9**.

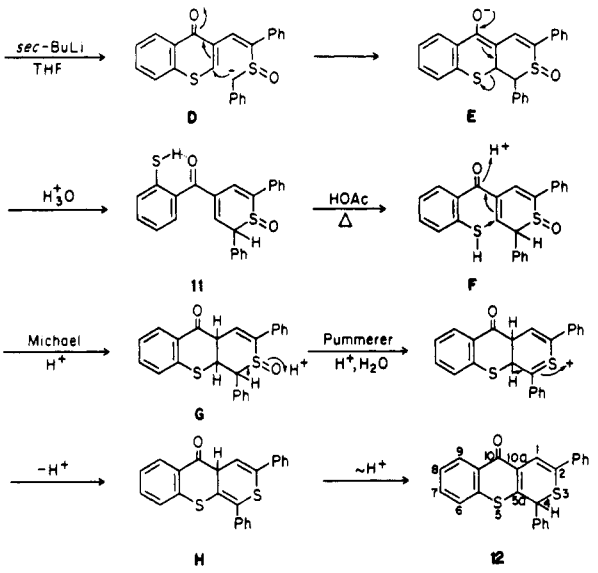


DBN in acetonitrile, a reagent which worked well in the thiopyrano[4,3-*c*]thiopyran series,[1] failed to yield any of the Michael adduct **10**. Instead, it appeared to have also added to the active vinylic sulfone double bond. The crude product isolated from aqueous workup had a complex ^1H NMR spectrum in which the alkyl absorptions due to DBN were detected at δ 1.8–3.8. Further evidence was derived

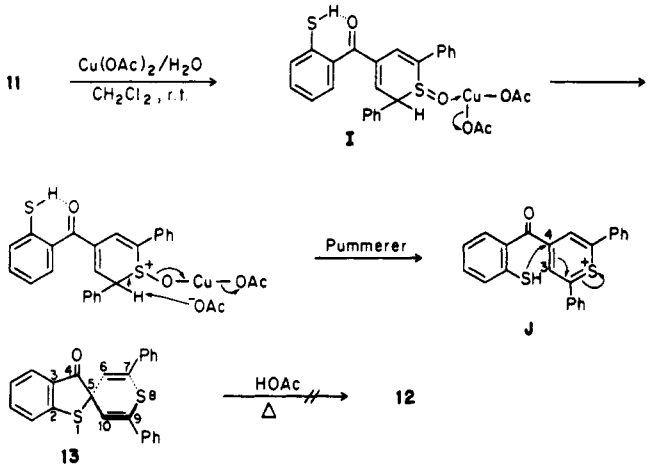
(3) Chen, C. H. *Tetrahedron Lett.* **1976**, 25.

(4) Rathke, M. W.; Kow, R. *J. Am. Chem. Soc.* **1972**, *94*, 6854. Olofson, R. A.; Dougherty, C. M. *Ibid.* **1973**, *95*, 581, 582.

Scheme III



Scheme IV



from its field desorption mass spectrum [m/e 592 M^+ for $C_{31}H_{32}N_2O_6S_2$ and 547 ($M^+ - H_2O$)], which revealed the incorporation of 1 molecule of DBN and H_2O.

Ring Closure of the Sulfoxide 6. Synthesis of 2,4-Diphenyl-4*H*-benzo[*e*]thiopyrano[3,4-*b*]thiopyran-10-one (12). Treatment of the sulfoxide **6** with 1.2 equiv of *sec*-BuLi or LDA in THF at room temperature followed by aqueous acid workup precipitated a yellow, fluorescent, *very insoluble* solid in about 84% yield after drying and washing with ether. The extreme insolubility of this compound in most organic solvents greatly hampered our efforts to purify it by recrystallization or chromatography. Spectroscopic characterizations were limited to those obtainable in the solid state. The IR spectrum (KBr pellet) of this product has a strong broad sulfoxide band at 1000–1030 cm^{-1},[5] and the broad band at 1600 suggests a hydrogen-bonded carbonyl. The mass spectrum (electron impact) showed a major molecular ion at m/e 402 for $C_{24}H_{18}O_2S_2$, which is isomeric with **6**. This compound reacted with pyidine-d_5 at room temperature to give a dark red solution from which no identifiable signals were obtained by ^1H NMR. Attempts to dissolve the solid in Me_2SO-d_6 by prolonged sonication (at 50–60 °C) also appeared to induce rearrangement, but none of the products were readily discernible by solution ^1H NMR spectroscopy. A structure that best fits the limited data at hand is tentatively assigned as **11**,[6] which is expected to be formed from the lithiated anion D by an addition–elimination mechanism involving the relatively stable vinylsulfinyl enolate E proposed in Scheme III.

Heating **11** in glacial acetic acid on a steam bath gave a deep red solution from which a light brown solid slowly crystallized on cooling (87% yield). The same compound was also obtained by reacting **11** with BF_3 etherate at room temperature. This product has been fully characterized as the desired thiopyrano[3,4-*b*]thiopyran-4-one **12** (m/e 384 M^+ for $C_{24}H_{16}OS_2$), apparently formed by loss of H_2O from **11**. The conjugation of the 5a double bond with the ketone is supported by the IR and ^1H NMR spectra, with the carbonyl band at 1620 cm^{-1} and the benzylic H_4 at δ 5.0 as a singlet. Owing to a deshielding effect of the carbonyl at C-10, the vinylic H_1 and the peri H_9 are shifted dramatically downfield to δ 7.73 (s) and 8.5 (m), respectively.

One possible mechanism for the formation of **12** under acid catalysis is proposed in Scheme III. The 5a,10a-dihydro intermediate G presumably forms first by an intramolecular Michael addition of the mercaptan to the α,β-unsaturated ketone function, which is also activated by conjugation with the electron-withdrawing sulfinyl group. Subsequent dehydration via a Pummerer-type of rearrangement of sulfoxides under acidic conditions is well precedented.[7] Prototropic shift of the initially formed 10aH compound H to yield the somewhat more stable thiochromone **12** is expected on thermodynamic grounds. An alternative pathway involving first the Pummerer rearrangement followed by an intramolecular Michael addition to an incipient thiopyrylium intermediate such as J (see Scheme IV) is not likely because we did not detect any formation of the spirothiopyran **13**, which was formed selectively under the influence of a very mild Lewis acid (see below).

Synthesis of 7,9-Diphenylbenzo[*b*]-1,8-dithiaspiro-[4,5]deca-6,9-dien-4-one (13). Stirring a suspension of **11** in methylene chloride with a small amount of 1% cupric acetate in water at room temperature caused **11** to dissolve slowly. The blue aqueous phase gradually turned greenish and then light brown. From the organic phase, we isolated in 50% yield a new product to which we assigned the spiro structure **13**. The carbonyl band at 1700 cm^{-1} (IR) and the equivalent H_6 and H_{10} at δ 5.92 as a singlet in the ^1H NMR spectrum of this new compound are in full agreement with the spirothiopyran structure **13**. Further confirmation comes from its ^{13}C NMR spectrum, which has only one sp^3 carbon (δ 66.09, s, quaternary) and the carbonyl is at δ 202.08. A compound of similar structure was characterized in our earlier work on the synthesis of the thiopyran[4,3-*c*]thiopyran system.[1]

The formation of **13** can be rationalized by the mechanism proposed in Scheme IV. Cupric acetate, being a mild electrophile, presumably reacted with the sulfoxide **11** to give I, which can undergo a Pummerer rearrangement to generate the thiopyrylium J, cupric oxide, and acetate ion. The formation of CuO was supported by the light brown color observed as the reaction proceeded. The highly electrophilic thiopyrylium J can be captured intramolec-

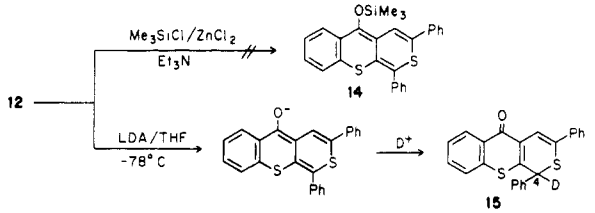
(5) The S=O stretching normally is found in the region around 1030–1050 cm^{-1} in solution. A shift of 10–20 cm^{-1} toward lower frequencies is not uncommon in the solid state. See: Cymerman, J.; Willis, J. B. *J. Chem. Soc.* **1951**, 1332.

(6) Owing to the lack of S–H stretching observed in the 2600-cm^{-1} region, we cannot rule out the possibility of a hemithioacetal structure that is polymeric. We thank the reviewer for this suggestion.

(7) Russell, G. A.; Mikol, G. J. "Mechanism of Molecular Migrations"; Thyagarojan, B. S.; Ed.; Interscience: New York, 1969; Vol. 2, pp 57–207.

ularly by the mercaptan group at the C-4 position to yield the spirothiopyran **13**. For J to form the desired thiopyrano[3,4-*b*]thiopyran **12**, it must first Michael add at the 3-position, which apparently is a very slow process under the reaction conditions. Furthermore, **13** is stable on heating with glacial acid, which also suggests that the ipso cyclization of J is irreversible and that there is no common intermediate between this pathway and that of Scheme III, which gives the thiopyran[3,4-*b*]thiopyran **12**.

Thiopyrano[3,4-*b*]thiopyran-4-one **12** cannot be readily enolized and captured as the trimethylsilyl enol ether under normal conditions.[8] However, it can be lithiated



by LDA in THF at −78 °C to give a dark brown solution of the corresponding enolate, which appears to be quite stable below about −20 °C. On quenching with deuterium oxide, the C-4 deuterated compound **15** was formed exclusively, as shown by its ^{1}H NMR spectrum, which is superimposable with that of **12** except the H_4 at δ 5.0 is absent.

Experimental Section

Melting points, obtained on a Thomas-Hoover melting-point apparatus, are uncorrected. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on Varian EM-390 and Bruker WH-270 spectrometers, with Me_4Si as the internal standard. Mass spectra were obtained on an AEI MS-30 mass spectrometer. Field-desorption mass spectra were recorded on a Varian MAT-731 spectrometer. IR spectra were obtained on a Beckman IR 4250 spectrophotometer. Elemental analyses were done by the Analytical Sciences Division, Kodak Research Laboratories.

3-[2(*Z*)-(Benzylthio)-2-phenylethenyl]-4*H*-thiochroman-4-one (5). To a solution of 14.62 g (0.0417 mol) of diethyl α-(benzylthio)benzylphosponate (**4**) in 100 mL of dry THF was added 28.5 mL of *n*-BuLi (1.6 M in hexanes) at −78 °C under argon. The resulting Wittig–Horner reagent was added dropwise at −55 to −65 °C to a solution of 7.7 g (0.0405 mol) of 3-formyl-4*H*-thiochroman-4-one (**3**) in 350 mL of THF over 30 min. The reaction mixture was equilibrated to ambient temperature overnight, poured into aqueous NH_4Cl and brine, and extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated to give 17 g of a brown viscous oil, which was crystallized from 300 mL of MeOH, giving 12.6 g (81% based on **3**) of **5**: mp 101–102 °C; IR (KBr) 1620 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.57 (s, 2, $PhCH_2$), 6.9–7.75 (m, 14, Ar H and olefinic), 8.06 (s, 1, olefinic), 8.45 (m, 1, Ar H); ^{13}C NMR ($CDCl_3$) δ 37.7 (d, sp^3 benzyl), 178.6 (s, C=O); mass spectrum, *m/e* 386 (M^+), 295 ($M^+ - C_7H_7$), 263 ($M^+ - C_7H_7S$). Anal. Calcd for $C_{24}H_{18}OS_2$: C, 74.6; H, 4.7; S, 16.6. Found: C, 74.4; H, 4.7; S, 16.2.

3-[2(*Z*)-(Benzylsulfinyl)-2-phenylethenyl]-4*H*-thiochroman-4-one (6). A solution of 3 g (1 equiv) of commercial grade *m*-chloroperbenzoic acid (87% active) in 150 mL of methylene chloride was added dropwise to an ice-cooled solution of 6 g (5.18 mmol) of **5** in 100 mL of methylene chloride over 30 min. The reaction was quenched immediately with saturated aqueous sodium bicarbonate, and the methylene chloride solution was separated, dried ($MgSO_4$), and concentrated. The solid residue was recrystallized from 400 mL of benzene and hexanes (2:3 v/v) to give 6 g (96%) of **6** as colorless fine needles: mp 161–162 °C dec; IR (KBr) 1620 (C=O), 1020, 1030 (S=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.95 (q, *J* = 12 Hz, 2, $PhCH_AH_B$), 7.1–7.8 (m, 15, Ar H and olefinic), 8.46 (m, 1, Ar H); mass spectrum, *m/e* (relative intensity) 402 (M^+), 263 (100). Anal. Calcd for $C_{24}H_{18}O_2S_2$: C, 71.6; H, 4.5. Found: C, 71.8; H, 4.7.

3-[2(*Z*)-Benzylsulfonyl)-2-phenylethenyl]-4*H*-thiochroman-4-one (8). A solution of 1.6 g (2 equiv) of MCPBA (87% active) in 50 mL of methylene chloride was added quickly at ambient temperature to a solution of 1.5 g (3.89) mmol) of **5** in 30 mL of methylene chloride. The reaction mixture was stirred overnight, washed with aqueous sodium bicarbonate, dried ($MgSO_4$), and concentrated. The solid residue was recrystallized from 100 mL of acetonitrile, from which 1.2 g (74%) of pure monosulfone derivative **8** was obtained: mp 196–197 °C; IR (KBr) 1600 (C=O), 1110, 1300 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.06 (s, 2, $PhCH_2$), 7.05–7.65 (m, 14, Ar H and olefinic), 8.03 (s, 1, olefinic), 8.5 (m, 1, peri Ar H); mass spectrum, *m/e* 263 ($M^+ - PhCH_2SO_2$). Anal. Calcd for $C_{24}H_{18}O_3S_2$: C, 68.9; H, 4.3; S, 15.3. Found: C, 69.0; H, 4.3; S, 14.9.

3-[2-(Benzylsulfonyl)-2-phenylethenyl]-4*H*-thiochroman-4-one 1,1-Dioxide (7). To a solution of 1.02 (2.66 mmol) of **5** in 10 mL of methylene chloride was added dropwise 30 mL of 40% peracetic acid. The reaction mixture was warmed overnight in an oil bath kept at 40–45 °C, poured into water, and salted out with NaCl. The light yellow precipitate was collected, washed with water, and air-dried to give 820 mg (69%) of crude disulfone **7**. FD mass spectrum, *m/e* 450 (M^+ for $C_{24}H_{18}O_5S_2$), 386 ($M^+ - SO_2$); IR (KBr) 1675 (C=O), 1310, 1115 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.4 (s, 2, $PhCH_2$), 6.36 (d, *J* = 1.8 Hz, 1, vinylic), 6.8 (d, *J* = 1.8 Hz, 1, vinylic), 7.1–8.3 (m, 14, Ar H); ^{13}C NMR ($CDCl_3$) δ 59.49 (t, sp^3, $PhCH_2$), 123.23, 126.56, 128.69, 128.85, 128.96, 129.02, 129.15, 129.72, 130.39, 131.23, 133.04, 133.18, 134.61, 134.83, 138.77, 140.77, 145.91, 177.63 (C=O).

3-[2-(Benzylsulfonyl)-1-(isopropyloxy)-2-phenylethyl]-4*H*-thiochroman-4-one 1,1-Dioxide (9). The crude disulfone **7**, on recrystallization from isopropyl alcohol, was converted to the Michael adduct **9**: mp 245–246 °C dec; FD mass spectrum, *m/e* 510 M^+; IR (KBr) 1670 (C=O), 1320 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.46 (dd, 6, 2 CH_3), 3.63 (AB q, 2, $PhCH_AH_B$), 4.4 (d, 1, PhCH), 4.5 (quint, 1, -$OCHMe_2$), 5.29 (d, 1, -OCH-), 6.9–8.2 (m, 14, Ar H), 8.02 (s, 1, vinylic). Anal. Calcd for $C_{27}H_{26}O_6S_2$: C, 63.5; H, 5.1; S, 12.5. Found: C, 63.1, H, 5.1, S, 12.2.

2,6-Diphenyl-2*H*-4-(2-mercaptobenzoyl)thiopyran 1-Oxide (11). To a solution of 3.2 g (7.96 mmol) of **6** in 200 mL of dry THF was added dropwise 6.82 mL (1.2 equiv) of *sec*-BuLi (1.4 M in cyclohexane) at room temperature under argon. The cherry-red solution was stirred overnight and poured into 400 mL of 1 N H_2SO_4; the precipitated yellow solid was filtered, washed with water, and air-dried. This solid was stirred with ether (400 mL) and filtered to give 2.7 g (84%) of crude product, which was insoluble in most organic solvents: mass spectrum, *m/e* 402 M^+, 385 ($M^+ - H_2O$), 264 ($M^+ - PhCH_2SO$); IR (KBr) 3000–3600 (br), 1000–1030 (strong, S=O), 1600 (br, medium, C=O), 1590 (C=C) cm^{-1}.

2,4-Diphenyl-4*H*-benzo[*e*]thiopyrano[3,4-*b*]thiopyran-10-one (12). Heating 800 mg (1.99 mmol) of crude **11** in 30 mL of glacial acetic acid on a stream bath produced a deep red solution from which 670 mg (87%) of **12** crystallized on standing overnight at room temperature: mp 160–161 °C; IR (KBr) 1620 (C=O) cm^{-1}; mass spectrum, *m/e* 384 M^+; ^{1}H NMR ($CDCl_3$) δ 5.0 (s, 1, H_4 benzylic), 7.15–7.7 (m, 13, Ar H), 7.73 (s, 1, H_1 vinylic), 8.5 (m, 1, peri Ar H). Anal. Calcd for $C_{24}H_{16}OS_2$: C, 75.0; H, 4.2; S, 16.7. Found: C, 74.7; H, 4.3; S, 16.3.

7,9-Diphenylbenzo[*b*]-1,8-dithiaspiro[4,5]deca-6,9-dien-4-one (13). A suspension of 150 mg (0.36 mmol) of the crude *seco*-sulfoxide **11** in 50 mL of methylene chloride and 10 mL of 1% cupric acetate in water was stirred at room temperature for 5 h. The solid slowly dissolved, and the blue color of aqueous Cu^{2+} slowly faded and turned light brown. The organic phase was separated, dried ($MgSO_4$), and evaporated on a rotary evaporator. The residue was recrystallized from 10 mL of acetonitrile to give 70 mg (50%) of **13**: mp 209–210 °C (needles); IR (KBr) 1700 (C=O) cm^{-1}; mass spectrum, *m/e* 384 M^+; ^{1}H NMR ($CDCl_3$) δ 5.92 (s, 2, vinylic), 7.23–7.63 (m, 13, Ar H), 7.82 (d, *J* = 7.8 Hz, 1, peri H); ^{13}C NMR ($CDCl_3$) δ 66.09 (s, quaternary sp^3), 113.80 (d), 123.78 (d), 125.66, 126.74, 127.72, 128.13, 128.74, 129.20, 136.66 (d), 137.58 (s), 137.93 (s), 151.53, 202.08 (s, C=O). Anal. Calcd for $C_{24}H_{16}OS_2$: C, 75.0; H, 4.2, S, 16.7. Found: C, 75.3; H, 4.3; S, 16.5.

(8) Danishefsky, S.; Kitahara, T. *J. Am. Chem. Soc.* **1974**, *96*, 7807.

X-ray Analysis. A suitable crystal of **8**, 0.25 × 0.25 × 0.13 mm, was obtained by slow recrystallization from acetonitrile. All data were taken at 22 (1) °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters obtained by refinement of the setting angles for 25 reflections with $11 < 2\theta < 25°$ were $a = 16.930$ (5) Å, $b = 17.248$ (2) Å, $c = 6.974$ (1) Å, $\beta = 100.51$ (1)°, $V = 2002$ (1) Å^3, $d_c = 1.388$ g cm^{-3}, and $Z = 4$. The space group was confirmed as $P2_1/n$ by collection and examination of the systematically absent reflections $h0l$, $h + l$ odd and $0k0$, k odd.

Intensity data were collected out to a limit of $2\theta < 50°$ by the Ω–2θ method at a variable scan rate from 3 to 20° 2θ min^{-1}. The scan range was from 2θ(Mo Kα_1) – 0.5° to 2θ(Mo Kα_2) + 0.5°. three standard reflections were remeasured periodically and showed no significant change. Corrections were made for Lorentz and polarization effects, but no absorption correction was necessary ($\mu = 2.86$ cm^{-1} for Mo Kα).

The structure was solved by direct methods with the program MULTAN79.[9] By use of 216 reflections with $E \geq 1.94$, an E map, calculated with the phase set having the best combined figure of merit, yielded 26 of the 29 non-hydrogen atoms. The remaining three atoms and all hydrogen atoms were located in subsequent difference electron density maps.

Refinement was by full-matrix least squares. The function minimized was

$$\Sigma w(|F_o| - K|F_c|)^2$$

where $w^{-1} = \sigma^2(F_o) + (0.03F_o)^2$. Scattering factors and anomalous dispersion corrections for all atoms were from International Tables for X-ray Crystallography.[10] The agreement indices are $R = \Sigma||F_o| - K|F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - K|F_c|)^2/\Sigma wF_o^2)^{1/2}$. Refinement proceeded smoothly and converged to $R = 0.036$ and $R_w = 0.049$ for the 29 non-hydrogen atoms with anisotropic thermal parameters and 18 hydrogen atoms with isotropic thermal parameters. Of the 3517 reflections measured, 2830 had $I > \sigma(I)$ and were included in the calculations. The estimated standard deviation of an observation of unit weight was 1.24. The final scale factor was 2.364 (6). A final difference electron density map contained residual density between –0.36 and +0.27 e/Å^3 but was featureless.

Registry No. **3**, 70940-99-7; **4**, 70660-17-2; **5**, 93454-57-0; **6**, 93454-58-1; **7**, 93454-59-2; **8**, 93454-60-5; **9**, 93454-61-6; **11**, 93454-62-7; **12**, 93454-63-8; **13**, 93454-64-9; *i*-PrOH, 67-63-0.

Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

(9) Computer programs used for this study were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975, revision 3B, 1980, except this version of MULTAN is from the 1981 SDP user's group tape exchange.

(10) "International Tables fof X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, Chapter 2.

An Alternate Synthesis of Cyclic 1,3-Dinitramines

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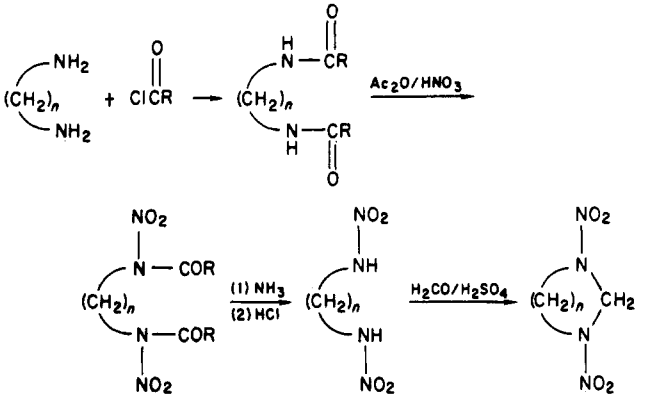
An alternate synthesis for cyclic 1,3-dinitramines has been developed. The new method involves the trapping of an in situ generated cyclic aminal with nitrous acid to generate a cyclic 1,3-dinitrosamine, which is subsequently converted to the cyclic 1,3-dinitramine by treatment with 100% nitric acid or solutions of N_2O_5 in 100% nitric acid. This alternate synthesis is superior for the synthesis of 5- and some 6-membered cyclic 1,3-dinitramines but not for 7-membered compounds.

Introduction

Cyclic 1,3-dinitramines are a potentially important class of energetic materials related to 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX). The first synthesis of a compound of this class was accomplished by Goodman[1] who synthesized 1,3-dinitro-1,3-diazacyclopentane, **1**, from ethylenediamine by the four-step procedure summarized in Scheme I. The same reaction sequence was used by Bell and Dunstan[2] to synthesize both 1,3-dinitro-1,3-diazacyclohexane, **2**, and 1,3-dinitro-1,3-diazacycloheptane, **3**. We have come to refer to this procedure as the "primary nitramine" synthesis of cyclic 1,3-dinitramines.

This procedure, although quite straightforward, suffers from two major problems. First, it requires four discrete steps which means that it is quite time consuming and that the overall yields are frequently not very high. Secondly, when we attempted to apply this procedure to the synthesis of more complicated polynitramines, such as the spirocyclic tetranitramine **4**, the yields for the ring closure step frequently were under 10%. It is well-known that primary nitramines are unstable in strong acid,[3] and it appears that in these cases the ring closure step is slower than the acid-catalyzed decomposition of the primary nitramine reactant.

Scheme I. Primary Nitramine Synthesis of Cyclic 1,3-Dinitramines[a]



[a] $n = 2, 3, 4$.

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(1) Goodman, L. *J. Am. Chem. Soc.* **1953**, *75*, 3019.
(2) Bell, J. A.; Dunstan I. *J. Chem. Soc. C* **1966**, 870.
(3) Fridman, A. L.; Ivshin, V. P.; and Novikov, S. S. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 640.