identification of the liverwort and Dr. K. Toriumi of the Institute for Molecular Science for valuable assistance with the X-ray work. Acknowledgement is made to the Institute for Molecular Science for use of a Rigaku four-circle diffractometer. Calculations were performed at the Kyoto University Computing Center and the computer room at the Tokushima Bunri University. Work at the Florida State University was supported in part by a grant (CA-13121) from the United States Public Health Service through the National Cancer Institute.

Registry No. 2, 63599-46-2.

Supplementary Material Available: Tables I–V listing final atomic parameters, bond lengths, and angles (5 pages). Ordering information is given on any current masthead page.

Synthesis of 2-Phenyl-4*H*-thiopyran-4-one

Chin H. Chen,* Jeffrey J. Doney, and George A. Reynolds

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

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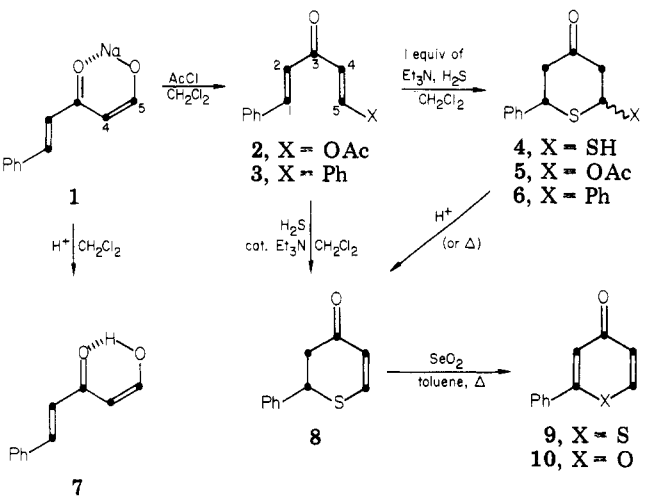
2-Phenyl-4*H*-pyran-4-one (**10**) has been prepared by acid-catalyzed cyclization of the appropriate phenylacetylenic β-keto aldehyde[1] or of (1*E*,4*E*)-5-hydroxy-1-methoxy-5-phenylpenta-1,4-dien-3-one,[2] or via the condensation of the boron difluoride complex of benzoylacetone and dimethylformamide dimethyl acetal.[3] None of these methods, however, is adaptable to the preparation of the thio analogue, 2-phenyl-4*H*-thiopyran-4-one (**9**),[4] which is a key intermediate desired for the synthesis of various *unsymmetrical* $\Delta^{4,4'}$-bis(4*H*-thiopyran) donors[5] with an unsubstituted C-2 position adjacent to sulfur. We now report a method that allows both **9** and its dihydro derivative, **8**, to be readily synthesized from the commercially available methyl styryl ketone.

Formylation of methyl styryl ketone with ethyl formate in the presence of sodium ethoxide in ethanol gave the sodium enolate **1** in 71% yield.[6] The 4*Z* configuration of **1** was established on the basis of its ^{1}H NMR spectrum (Me_2SO-d_6), which has a doublet at δ 4.9 ppm for the C-4 proton with cis coupling of $J_{4,5}$ = 9.75 Hz. Acetylation of **1** with 1 equiv of acetyl chloride in methylene chloride gave the corresponding enol acetate **2** (77% yield), which was assigned the 1*E* and 4*E* stereoconfigurations based on the relatively large, apparent trans H–H coupling constants $J_{1,2}$ = 15.75 and $J_{4,5}$ = 12.75 Hz.[7] (See Scheme I.) The corresponding enol **7**, which was easily prepared by acidification of a methylene chloride suspension of **1** with dilute hydrochloric acid, has a doublet at δ 5.65 ppm for the C-4 proton with cis $J_{4,5}$ = 3 Hz and a doublet at δ 6.45 ppm with a typical trans $J_{1,2}$ = 16.5 Hz as measured.

Scheme I



Compound **2** was not stable to heat. Although **2** could be purified by recrystallization, it was best used immediately without isolation to avoid troublesome decomposition. A solution of the crude enol acetate **2** and a catalytic amount of triethylamine in methylene chloride was saturated with a slow stream of hydrogen sulfide at ambient temperature, giving 5,6-dihydro-6-phenyl-4*H*-thiopyran-4-one (**8**) in 59% yield based on the sodium enolate **1**. This base-catalyzed hydrogen sulfide cyclization of **2** presumably follows the same course as that of 1,5-diphenyl-1,4-pentadien-3-one (**3**) in the preparation of 2,6-diphenyl-4*H*-tetrahydrothiopyran-4-one (**6**).[8] The intermediate, 2-acetoxy-6-phenyl-4*H*-tetrahydrothiopyran-4-one (**5**) formed in situ, apparently was not stable under the experimental conditions, which caused the elimination of acetic acid to produce directly the dihydro derivative **8**. Dehydrogenation of **8** with selenium dioxide in refluxing toluene[9] gave the desired product **9** in 85% yield.

In the presence of 1 equiv of triethylamine, the hydrogen sulfide addition to **2** gave a different product, to which we assigned the structure 2-mercapto-6-phenyl-4*H*-tetrahydrothiopyran-4-one (**4**) on the basis of its spectroscopic data. These include the high-resolution mass spectrum, which shows a molecular ion at *m/e* 224.0343 (calcd for $C_{11}H_{12}OS_2$, 224.0344), and its IR spectrum, which has a $\nu_{C=O}$ at 1710 cm^{-1} that is typical of the carbonyl stretching of a tetrahydro-4*H*-thiopyran-4-one such as **6**.[9] The crude **4**, which has a strong mercaptan odor, was not purified, owing to its lability toward heat, which caused the elimination of hydrogen sulfide to give **8** (shown by the change in the ^{1}H NMR spectrum of **4** heated in an NMR tube at ca. 100 °C). The mercaptan **4** was also unstable toward acid. Thus, on addition of excess trifluoroacetic acid at room temperature, **4** was quickly converted to **8**, which was isolated, upon usual workup, in 55% yield. The formation of **4** from **2** can be attributed to a secondary Michael reaction between the initial product **8** formed in situ and hydrogen sulfide anion, which is present in relatively high concentration. This was confirmed in a separate experiment by treating **8** with excess hydrogen sulfide and 1 equiv of triethylammonium acetate in methylene chloride at room temperature for 24 h, from which 60% of **4** was

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detected by ^1H NMR along with ca. 40% of unreacted 8.

Experimental Section

Melting points, obtained on Mettler FPI and Mel-Temp instruments, are uncorrected. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer, and ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer with Me_4Si as internal standard. Mass spectra were obtained on an AEI MS-30 mass spectrometer. IR spectra were recorded on a Beckman IR 4250 spectrometer. Elemental analyses were done by the Analytical Sciences Division, Kodak Research Laboratories.

(1*E*,4*E*)-5-Acetoxy-1-phenylpenta-1,4-dien-3-one (2). Acetyl chloride (0.85 g, 0.011 mol) was added dropwise to a suspension of 2 g (0.01 mol) of sodium cinnamoylacetaldehyde (1)[6] in ca. 75 mL of methylene chloride at room temperature. After 3 h of stirring, some anhydrous potassium carbonate was added, and the mixture was filtered and evaporated at 35–40 °C to give 3.3 g (77%) of crude 2 as a red oil that slowly solidified at room temperature. This compound was not stable on storage and was used immediately without further purification: ^1H NMR ($CDCl_3$) δ 2.2 (s, 3 H, OAc), 6.27 (d, 1 H, $J_{4,5}$ = 12.75 Hz, C-4 olefinic), 8.34 (d, 1 H, $J_{4,5}$ = 12.75 Hz, CHOAc), 6.83 (d, 1 H, $J_{1,2}$ = 15.75 Hz, C-1 olefinic), 7.58 (d, 1 H, $J_{1,2}$ = 15.75 Hz, C-2 olefinic), 7.2–7.6 (m, 5 H, arom); ^{13}C NMR ($CDCl_3$) δ 20.3 (CH_3CO_2), 113.0 (C-4), 125.3 (C-4′ of Ph), 128.9, 128.4 (C-2′, C-3′ of Ph), 130.5 (C-2), 134.7 (C-1′ of Ph), 143.2 (C-1), 148.9 (C-5), 167.0 (C=O of OAc), 188.4 (C-3); IR (KBr) 1770 (ester C=O) and 1630 cm^{-1} (C=O of α,β-unsaturated ketone).

Recrystallization of 1.8 g of crude 2 from 250 mL of hexanes containing a small amount of benzene gave 200 mg of an analytical sample as a light-orange solid: mp 69–70 °C. Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.2; H, 5.6. Found: C, 72.2; H, 5.7.

5,6-Dihydro-6-phenyl-4*H*-thiopyran-4-one (8). A solution of 15.2 g (0.2 mol) of acetyl chloride in 50 mL of CH_2Cl_2 was added quickly to a well-stirred suspension of 40 g (0.2 mol) of sodium cinnamoylacetaldehyde 1[6] in 500 mL of CH_2Cl_2 at room temperature. The resulting dark-brown solution (containing a small amount of insoluble sodium chloride) was stirred for 5 h more, 10 drops of triethylamine was added, and the mixture was saturated with H_2S (40 min). The reaction mixture was stirred overnight and washed with water (3 × 400 mL). The organic phase was separated, dried ($MgSO_4$), and evaporated to give 37 g of crude 8 as a dark-red oil that slowly solidified at room temperature. The material was purified by short-path distillation [bp 120–121 °C (0.2 mm)], giving 22.7 g (59%) of 8 as a light-brown oil that solidified at room temperature. Slow recrystallization from benzene and hexanes in a freezer gave an analytical sample as colorless needles: mp 48–49 °C; IR (KBr) 1660 cm^{-1} (C=O); mass spectrum, m/e 190 (M^+); ^1H NMR ($CDCl_3$) δ 2.73–3.26 (m, 2 H, C-5 ring methylene), 4.64 (dd, 1 H, $J_{5,6}$ = 12.75 Hz, $J_{5',6}$ = 5.25 Hz, C-6 benzylic methine), 6.22 (d, 1 H, $J_{2,3}$ = 10.5 Hz, C-2 olefinic), 7.43 (d, 1 H, $J_{2,3}$ = 10.5 Hz, C-3 olefinic), 7.34 (s, 5 H, arom); ^{13}C NMR ($CDCl_3$) δ 44.9 (t, C-5 methylene), 46.9 (d, C-6), 123.5 (d, C-3), 127.4, 128.5, 129.0, 137.8 (Ph), 146.1 (d, C-2), 194.1 (s, C-4 carbonyl). Anal. Calcd for $C_{11}H_{10}OS$: C, 69.4; H, 5.3; S, 16.9. Found: C, 69.8; H, 5.3; S, 16.7.

2-Phenyl-4*H*-thiopyran-4-one (9). A mixture of 4.6 g (0.024 mol) of 8 and 3.2 g (0.028 mol, 1.2 equiv) of selenium dioxide in 125 mL of toluene was refluxed for 5 h, and the water was removed with a Dean–Stark trap. The reaction mixture was cooled and filtered, the filtrate was evaporated, and the solidified dark-red residue was purified by short-path distillation in vacuo to give 3.85 g (85%) of 9 [bp 175–185 °C (0.1 mm)], which solidified at room temperature to a light-brown solid. An analytical sample was obtained as light-brown needles by recrystallization from benzene/hexanes (1:2 v/v): mp 95.5 °C; IR (KBr) 1605 cm^{-1} (C=O); mass spectrum, m/e 188 (M^+), 160 (M^+ – CO); ^1H NMR ($CDCl_3$) δ 7.0 (dd, 1 H, $J_{5,6}$ = 10.2 Hz, $J_{3,5}$ = 1.5 Hz, C-5H), 7.15 (d, 1 H, $J_{5,3}$ = 1.5 Hz, C-3H), 7.73 (d, 1 H, $J_{6,5}$ = 10.2 Hz, C-6H), 7.47 (m, 5 H, arom); ^{13}C NMR ($CDCl_3$) δ 126.8, 129.3, 129.9, 136.0 (phenyl), 128.5 (d, C-3), 130.7 (d, C-5), 137.6 (d, C-6), 153.3 (s, C-2), 180.8 (s, C=O). Anal. Calcd for $C_{11}H_8OS$: C, 70.2; H, 4.3; S, 17.0. Found: C, 70.1; H, 3.9; S, 16.9.

(1*E*,4*Z*)-1-Phenyl-5-hydroxypenta-1,4-dien-3-one (*trans*-Cinnamoylacetaldehyde, 7). To a suspension of 610 mg (3.1 mmol) of 1 in 50 mL of methylene chloride at room temperature was added 50 mL of 2 N HCl. The reaction mixture was stirred for 2 h and extracted with ether (150 mL). The organic phase was separated, washed with brine, dried ($MgSO_4$), and evaporated to give 400 mg of dark-red solid that was not stable on keeping. The structure was confirmed spectroscopically: IR (KBr) 1615 (br, C=O), 1580 (C=O), 1640 (sh, C=O), 3500 cm^{-1} (br, OH); high-resolution mass spectrum, m/e 174.0674 (M^+ calcd for $C_{11}H_{10}O_2$, 174.0667); ^1H NMR ($CDCl_3$) δ 5.65 (d, $J_{4,5}$ = 3 Hz, 1 H, C-4 olefinic), 6.45 (d, $J_{1,2}$ = 16.5 Hz, 1 H, C-2 olefinic), 7.3–7.6 (m, 5 H, arom), 7.58 (d, $J_{1,2}$ = 16.5 Hz, 1 H, C-1 benzylic), 8.6 (d, $J_{4,5}$ = 3 Hz, 1 H, C-5 olefinic), 13.9 (very br s, 1 H, enol); ^{13}C NMR ($CDCl_3$) δ 102.1 (C-4), 122.8, 128.1, 128.5, 128.9, 130.2 (C-2), 134.9, 141.2 (C-1), 184.1 (C-3 carbonyl).

2-Mercapto-6-phenyl-4*H*-tetrahydrothiopyran-4-one (4). Acetyl chloride (3.2 g, 0.04 mol) was added at room temperature to sodium cinnamoylacetaldehyde (1; 8 g, 0.04 mol) in 250 mL of methylene chloride. The reaction mixture was stirred for 3 h, and 4.1 g (1 equiv) of triethylamine was added, followed by saturation with a steady stream of H_2S for ca. 4 h. This mixture was stirred overnight, washed with water, dried ($MgSO_4$), and evaporated to give 7.7 g (85%) of crude 4 as an odorous red oil that, on keeping in vacuo, slowly solidified at room temperature. This material was not purified because of its tendency to eliminate H_2S. The structure is supported by spectroscopic evidence: IR (KBr) 1710 cm^{-1} (C=O for tetrahydro-4*H*-thiopyran-4-one);[9] high-resolution mass spectrum, m/e (relative %) 224.0343 (M^+ calcd for $C_{11}H_{12}OS_2$ 224.0344, 1), 190.0443 ($M^+ - H_2S$, 45), 104.0660 ($PhCHCH_2^+$, 100); ^1H NMR ($CDCl_3$) δ 2.6–3.3 (m, 5 H, C-3, C-5 ring methylenes and SH, slowly exchangeable with deuterium in CD_3OD), 4.45–4.9 (m, 2 H, C-2, C-6 methines), 7.3 (br s, 5 H, arom); ^{13}C NMR ($CDCl_3$) δ 44.1 (d, C-2), 47.5 (t, C-5), 49.9 (d, C-6), 50.9 (t, C-3), 127.6, 128.3, 129.0 (C-1′, C-3′ Ph), 138.7 (C-4′ Ph), 204.8 (s, C-4 C=O).

To 1.7 g (7.6 mmol) of the crude 4 was added 50 mL of trifluoroacetic acid at room temperature. The solution immediately turned very dark and was stirred overnight. The solution was evaporated, and the residue was dissolved in CH_2Cl_2, washed with aqueous sodium bicarbonate followed by water, dried ($MgSO_4$), and evaporated to give a dark gum. The gum was short-path distilled at ca. 115 °C (0.3 mm) to give 800 mg (55%) of 8, characterized and confirmed by comparison with an authentic sample.

Registry No. 1, 78965-30-7; (1*E*,4*E*)-2, 78965-31-8; 4, 78965-32-9; (1*E*)-7, 78986-41-1; 8, 78965-33-0; 9, 78965-34-1.

Absolute Configurations and Rotations of *exo*- and *endo*-2-Methylbicyclo[3.2.1]oct-3-ene

Harlan L. Goering* and Steven S. Kantner[1]

Samuel M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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In another study it became important to know the absolute configuration and rotation of *exo*-2-methylbicyclo[3.2.1]oct-3-ene (3) and *endo*-2-methylbicyclo[3.2.1]oct-3-ene (6). This paper describes correlations that provide this information.

The optical configuration and rotation of 3 and 6 were correlated with *exo*-bicyclo[3.2.1]oct-3-en-2-ol (1-OH) as outlined in Scheme I. The absolute rotation for 1-OH (219°)[2,3] was originally determined by complete resolution and isotope dilution. In this work we have confirmed this

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