δ 7.6 (br s, H-1); MS, *m/e* calcd for $C_{17}H_{11}D$ 217.1002, found 217.1015.

General Photochemistry. For photochemical reactions, a Rayonet Srinivasan-Griffin Photochemical Reactor (Southern New England Ultraviolet Co.), equipped with a merry-go-round apparatus and 254-nm (RPR-2537*P*) lamps, was used. All irradiations were done in quartz tubes. The tubes were sealed with serum stoppers secured with copper wire, and the solutions were deoxygenated by bubbling N_2 through them for 25 min.

Direct Irradiation of 1-(Bromomethyl)-3,4:6,7-dibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (1-Br) in HOAc. Two matched quartz tubes were charged with 12.5 mL of a 0.062 M solution of 1-Br in glacial HOAc (prepared by dissolving 473 mg (1.6 mmol) of 1-Br in 25 mL of HOAc). After being sealed and deoxygenated, tube 1 was masked with aluminum foil to block out light to check for any possible ground-state reaction. Tube 2, similarly treated, was left unmasked. Both tubes were placed on the merry-go-round of the Rayonet. The tubes were irradiated for 30 min.

After irradiation, each tube was opened and the contents poured into 100 mL of ether and extracted with 100 mL of saturated brine. The brine layer was then extracted twice with 50 mL of ether. The ether fractions were combined and extracted twice with 100 mL of water, twice with 100 mL of brine, thrice with 100-mL portions of aqueous $NaHCO_3$, and twice with 100 mL of brine. The solution was then dried ($MgSO_4$) and filtered, and the ether was removed under reduced pressure.

^{1}H NMR analysis of the reaction mixture in tube 1 showed only 1-Br present. ^{1}H NMR analysis of tube 2 showed a mixture of about 20% of 3,4-benzofluorene (**2**) and 80% of 1-Br. No other products were seen. Column chromatography with hexanes on silica gel (60–200 mesh) gave 35 mg (0.16 mmol, 21% conversion based on starting amount of 1-Br) of **2**: mp 125–127 °C; ^{1}H NMR δ 8.85 (br d, 1 H, H-13, $J_{12,13}$ = 8 Hz), 8.46 (br d, 1 H, H-5, $J_{5,6}$ = 8 Hz), 8.1–7.2 (m, 8 H, aromatic protons), 4.01 (s, 2 H, H-9).

Direct Irradiation of 7-Br in HOAc. A solution of 205 mg (0.67 mmol) of **7**-Br in 12.5 mL of HOAc was deoxygenated and then irradiated for 1 h with 254-nm light in the Rayonet.

After irradiation, the tube was opened, and the contents were poured into 100 mL of ether and worked up as described for the 1-Br photoreaction. Workup as above gave 49.2 mg (0.23 mmol, 34% conversion) of **14**: mp 125–126.5 °C; ^{1}H NMR δ 8.85 (br d, 1 H, H-13, $J_{12,13}$ = 8 Hz), 8.45 (br d, 1 H, H-5, $J_{5,6}$ = 8 Hz), 8.1–7.2 (m, 7 H, aromatic protons), 4.02 (s, 2 H, H-9); ^{2}H NMR δ 7.74 (br s, H-1). The locus of the deuterium atom was determined by ^{2}H NMR analysis and comparison of the ^{1}H NMR spectrum with that reported[6] for **2**: MS, *m/e* calcd for $C_{17}H_{11}D$ 217.1002, found 217.1015.

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Registry No. 1-Br, 28545-62-2; **2**, 205-12-9; **7**-OH, 118418-32-9; **7**-Br, 118418-33-0; **14**, 118418-34-1.

2,5-Dihydroxythiophene

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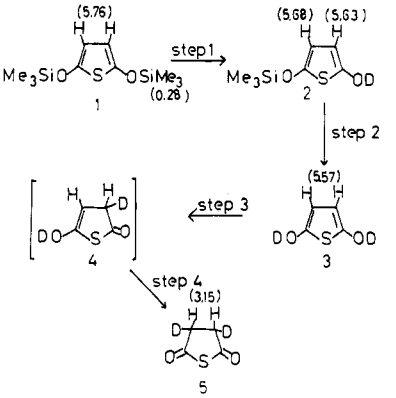
2,5-Dihydroxythiophene is the diene–diol tautomer of thiosuccinic anhydride. That the latter is the stable form was demonstrated by NMR and IR spectroscopy.[1] Recently we have shown that unstable enolic tautomers of heterocyclic compounds may be generated in solution by careful hydrolysis of their trimethylsilyl derivatives[2–4] and the ready availability of 2,5-bis[(trimethylsilyl)oxy]thiophene[5] led us to attempt to use this as a precursor for the generation of 2,5-dihydroxythiophene.

Scheme I



The ^{1}H NMR spectrum of 2,5-bis[(trimethylsilyl)oxy]thiophene in DMSO-d_6 at 30 °C shows two signals at δ = 0.28 and 5.76 (assigned as shown in Scheme I). This spectrum also shows that a small amount of hydrolysis has occurred as three small signals at δ = 5.55–5.7 are present. On addition of 1% of 7×10^{-4} M DCl in D_2O the two signals of the precursor almost completely disappeared immediately, but there was only a small signal at δ = 3.15, the chemical shift of the protons of thiosuccinic anhydride. Instead there were two small signals at δ = 5.68 and 5.63 and a larger signals at δ = 5.57. After 8 min the two small signal had disappeared completely but the singlet at δ = 5.57 remained, and over the course of 1 h this also disappeared with concurrent growth of the broad singlet of the deuterated thiosuccinic anhydride at δ = 3.15.

We suggest that these results can be explained by the reactions shown in Scheme I. The two signals at δ = 5.68 and δ = 5.63 were ascribed to the O-deuterated monohydroxythiophene (**2**). The ring protons should be a tightly coupled AB pair, so the signals at δ = 5.68 and 5.63 would be the large inner signals of the expected quartet. The signals presumably never became very large because the rates of removal of the two trimethylsilyl groups (steps 1 and 2 Scheme I are similar). The signal at δ = 5.57 was ascribed to the O-deuterated dihydroxy compound (**3**). Now the two ring protons are equivalent so that this signal is a singlet. There is no signal at δ = 0.28, showing that all the trimethylsilyl groups have been hydrolyzed and the chemical shift of the ring protons is slightly upfield as compared to the starting material. This is normally what happens to the chemical shift of the β-protons when a trimethylsilyl derivative is converted into its parent enol.[2–4] The species that is formed is clearly an intermediate on the conversion of **1** into the deuterated thiosuccinic anhydride (**5**), which is formed over the course of 1 h, and there seems to be no alternative structure to **3**. The monoenol **4** would be expected to be an intermediate in the conversion of **3** into **5**, but this was not detected. Unlike **3**, **4** is not aromatic and so would be expected to ketonize much more rapidly.

A similar series of experiments was carried out with 2,5-bis[(trimethylsilyl)oxy]furan[6] in an attempt to generate O-deuterated 2,5-dihydroxyfuran, but the results were not

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Scheme II

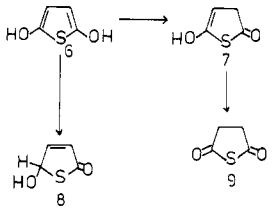

Table I. Rate Constants for the Ketonization of 2,5-Dihydroxythiophene and 2-Hydroxythiophene in Acetonitrile-Water Mixture (9:1 v/v) at 25 °C[a]

	k_{H^+},M^{-1} s^{-1}	$10^3 k_{H_2O}$,s^{-1}
2,5-dihydroxythiophene	7.46	4.5
2-hydroxythiophene[b]	0.21	1.02

[a] Ketonization with protonation at position 3. [b] B. Capon and F. C. Kwok, submitted for publication. Kwok, F. C. Ph.D. Thesis, University of Hong Kong, 1987.

so conclusive. The ^1H NMR spectrum of bis[(trimethylsilyl)oxy]furan in DMSO-d_6 at 30 °C showed signals at δ = 0.22 and 4.9. On addition of 8% of 7×10^{-5} M DCl in D_2O transient signals were observed at δ = 4.88, 4.82, and 4.76, but these were very small and had half-lives of about 1 min. The final spectrum was that of dideuteriosuccinic anhydride with a broad singlet at δ = 2.95. The transient signals observed in this experiment were all slightly upfield from the signal of the ring protons of the starting material and so could have been derived from intermediates that are analogous to those detected in the hydrolysis of 2,5-bis[(trimethylsilyl)oxy]thiophene.

The hydrolysis of 1-methyl-2,5-bis[(trimethylsilyl)-oxy]pyrrole[5] was also investigated under a variety of conditions, but no intermediates were detected, only the final product, the dideuterated *N*-methylsuccinimide.

Ketonization of 2,5-Dihydroxythiophene

The kinetics of ketonization of 2,5-dihydroxythiophene in an acetonitrile–water mixture (9:1 v/v) were studied by UV spectroscopy at a wavelength (255 nm) at which the dihydroxythiophene absorbed but at which the thiosuccinic anhydride did not. No evidence for the incursion of an intermediate was obtained and on the basis of the NMR spectroscopic results the monoenol 7 would not be expected to be detected. There is also the possibility of ketonization with protonation at position 5 to yield 8 (see Scheme II), but no evidence was found by UV or NMR spectroscopy for the formation of this or of its possible decomposition products.

The values of k_{obs} for the disappearance of 2,5-dihydroxythiophene were plotted against [H^+] to yield the values for k_{H^+} and k_{H_2O} given in Table I. It is seen that the 2,5-dihydroxythiophene ketonizes a little faster than would be expected from the rate constants for ketonization of 2-hydroxythiophene and the fact that it has two sites for attack.

Experimental Section

2,5-Bis[(trimethylsilyl)oxy]thiophene,[5] 2,5-bis[(trimethylsilyl)oxy]furan,[6] and 1-methyl-2,5-bis[(trimethylsilyl)oxy]pyrrole[5] were made by standard procedures as described in the references cited.

^1H NMR spectra were measured on a Varian EM 360 spectrometer. The spectra of solutions of the bis[(trimethylsilyl)oxy] derivatives in DMSO-d_6 were measured, the requisite amount of D_2O–DCl was added, and NMR spectra were recorded until reaction was complete.

The kinetic investigations were carried out in a thermostatted cuvette in the cell compartment of a Shimadzu UV-250 spectrophotometer which operated on-line with an Apple II microcomputer via an IEEE interface. A stock solution of 2,5-dihydroxythiophene in DMSO-d_6–D_2O (9:1 v/v) was prepared as described above and 20 μL were injected into 2 mL of the acetonitrile–water mixture (9:1 v/v) that contained HCl at the required concentration. Absorbance data were collected on-line at convenient time intervals and first-order rate constants were calculated by a generalized least-squares method.[7]

Registry No. 1, 91210-72-9; 2, 118631-17-7; 3, 118631-18-8; 5, 118631-19-9; 6, 118631-20-2; 9, 3194-60-3; 2,5-bis[(trimethylsilyl)oxy]furan, 77220-06-5; 3,4-dideuterosuccinic anhydride, 118631-21-3; 2-[(trimethylsilyl)oxy]-5-(deuteriohydroxy)furan, 118631-22-4; 2,5-bis(deuteriohydroxy)furan, 118631-23-5; 1-methyl-2,5-bis[(trimethylsilyl)oxy]pyrrole, 91210-73-0; 3,4-dideuterio-1-methylsuccinimide, 118631-24-6.

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Synthesis of Ethyl Thioformate and Thioformamides

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In 1963 Mayer and Berthold[1] showed that ethyl thioformate could be prepared from ethyl orthoformate by treatment with H_2S and a catalytic amount of sulfuric acid in acetic acid in 33% yield. Essentially the same procedure appeared in *Organic Syntheses*[2] in 1979 giving a 30–38% yield (with about 5% of the ethyl formate).

We have been able to improve the yield in this step and find that the crude product can be used in situ to prepare thioformamides. First the acetic acid was omitted since carboxylic acids are known to react with ethyl orthoformate to give ethyl esters.[3] Secondly, rather than H_2S being bubbled into the solution, the gas was introduced from a balloon reservoir. With that we observed that the absorption of gas ceased after about one-third of the expected amount. More sulfuric acid catalyst was then added, and absorption resumed immediately. Apparently ethyl sulfate formation consumes the catalyst.[4] Similar behavior was observed with concentrated HCl as catalyst;[5] however, 70% perchloric acid remained active to the end, affording a solution of ethyl thioformate in 77–83% yield along with 5–21% ethyl formate. We then added an equivalent of primary or secondary amine to the original flask and found rapid conversion to the thioformamide in 58–73% overall yields. This avoids the handling and workup of the malodorous intermediate.

Other methods for the preparation of thioformamides have been reviewed by Mills.[6] Purified ethyl thioformate has been used to prepare thioformamides.[7-9] By our

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