MHz spectrum of the 1,1,4,4-tetradeuterated derivative of **3** gives chemical shifts of δ 3.35, 2.48, and about 2.5 for H-4a, the methyl group, and H-10b, respectively, and coupling constants of $J_{4a,10b}$ = 4.6 and J_{4a,CH_3} = 2.4 Hz. By analogy, a similar correction seems in order for the proposed solution conformation of the parent 7,8,9-trimethoxy-4a,10b-*cis*-1,2,3,4,4a,10b-hexahydrophenanthridine.[8] The predominance of the conformation where H-4a is equatorial and H-10b axial is also consistent with the observed allylic coupling constant of about 3 Hz (presumably negative) between H-6 and H-4a.[8] Although the alternative conformation, where H-4a approaches coplanarity with the double bond, could lead to positive allylic coupling,[9] the deviation from coplanarity by about 20° should yield a coupling constant of somewhat smaller magnitude than that observed.

The incorporation of deuterium on carbons 1 and 4 of **3** was accomplished by using 1,3-butadiene-*1,1,4,4-d*$_4$[10] in the Diels–Alder condensation step of the synthetic scheme of **3**.[1,8,11] Incorporation of deuterium on the 4a position in **1a** was accomplished by base-catalyzed deuterium exchange on the *trans*-2-(3,4,5-trimethoxyphenyl)nitrocyclohexane intermediate[11] in a mixture of D_2O and tetrahydrofuran. The deuterated nitro compound was reduced to the corresponding amine with iron in acetic acid[12] and was found to contain about 90% deuterium at C-1 by NMR. The amine was converted to the deuterated analog of **1a** by the previously described procedure.[1]

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Registry No.—**1a**, 34035-53-5; **1b**, 34035-58-0; **2**, 34910-05-9; **3**, 34910-07-1.

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An Unusual 2,3-Disubstitution of Furan Ring

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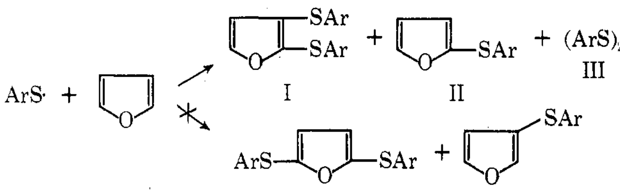
It is well known that furan can react with ionic[1] or radical[2] reagents, giving both substitution and 2,5-addition products; we wish now to report a case in which a 2,3-addition to the furan ring can explain the reaction products.

Furan was allowed to react with *p*-bromophenylthio radicals generated by H_2O_2/Fe^{2+} oxidation of the parent thiol in *tert*-butyl alcohol–water mixture under the conditions of the Fenton reaction.[3] The reaction products were 2,3-bis(*p*-bromophenylthio)furan (I) and 2-(*p*-bromophenylthio)furan (II) in 2:1 ratio; *p*-bromodiphenyl disulfide (III) was also separated. Gas chromatographic analysis of the reaction mixture indicates absence of 2,5-bis(*p*-bromophenylthio)furan or 3-(*p*-bromophenylthio)furan (Scheme I).

Scheme I

$$H_2O_2 + H^+ + Fe^{2+} \longrightarrow HO\cdot + H_2O + Fe^{3+}$$

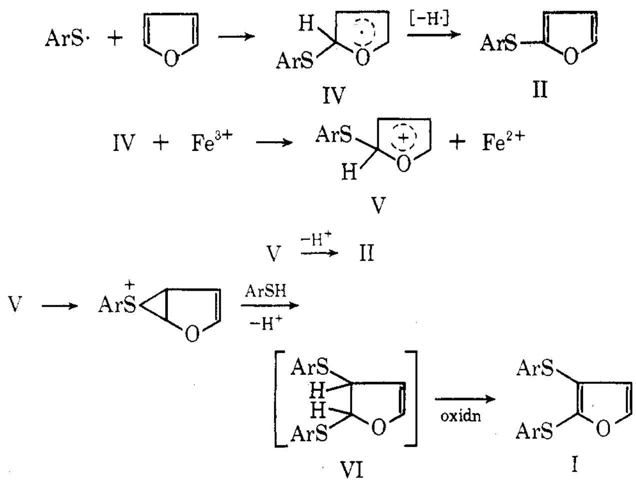
$$ArSH + \cdot OH \longrightarrow ArS\cdot + H_2O$$



Thio aryl radicals were also generated in furan by hydrogen abstraction with *tert*-butoxy radicals from *p*-bromothiophenol or by cumene hydroperoxide initiated autoxidation[4] of *p*-bromothiophenol; in these cases the only addition product formed was II in low yields.

The products of the Fenton reaction can reasonably be rationalized by a mechanism involving the oxidation of the α complex IV by ferric ions, the cation V formed then reacting with a molecule of thiophenol giving the dihydro derivative VI, readily dehydrogenated to I (Scheme II).

Scheme II



The attack of thiophenol at position 3 of the cation V can be explained by the participation of the lone pair of the sulfur atom attached to the ring; this effect is well known in other systems.

We believe that the fully homolytic pathway that could be devised to explain the formation of I (Scheme III) is not realistic because of the lack of formation of I in the reaction carried out in the absence of ferric ions. In this case, in fact, the only product is the "normal" 2-substitution product

Scheme III

$$IV + PhS\cdot \longrightarrow [VI] \xrightarrow{R\cdot} I + RH$$

(II). This is in agreement with the experimental results available in the literature,[5] where no evidence can be found to consider that β-arylthio radicals are bridged.

Compound I could be formed by further substitution on II, but when II was allowed to react under the conditions of the Fenton reaction, no I was identified in the reaction mixture.

Experimental Section

2-(*p*-Bromophenylthio)furan (II). To a solution of *n*-butyllithium [prepared from *n*-butyl bromide (2.29 g) and lithium (0.297 g) in dry ether] was slowly added at −30° 2-iodofuran[6] (3.68 g) in dry ether. The solution was allowed to reach ambient temperature and stirred for 2 hr. The reaction mixture was then cooled again at −70° and 4,4′-dibromodiphenyl disulfide (8.04 g) in dry ether was added. The reaction mixture was left overnight without further cooling, then hydrolyzed with HCl (10%). From the ethereal layer, after concentration and vacuum distillation, was obtained 2-(4-bromophenylthio)furan (3.1 g), bp 120° (0.5 mmHg). Anal. Calcd for $C_{10}H_7BrOS$: C, 47.07; H, 2.77; S, 12.57; Br, 31.32. Found: C, 47.8; H, 3.0; S, 12.8; Br, 32.0.

Oxidation with H_2O_2 in acetic acid gave the corresponding sulfone, mp 123–124°. Anal. Calcd for $C_{10}H_7BrO_3S$: C, 41.81; H, 2.44; S, 11.15; Br, 27.87. Found: C, 41.7; H, 2.3; S, 11.3; Br, 27.6.

In the same way (from *n*-butyllithium, 3-iodofuran,[7] and 4,4′-dibromodiphenyl disulfide) was prepared 3-(*p*-bromophenylthio)furan, bp 110° (0.5 mmHg) (Anal. Found: C, 47.5; H, 2.81; S, 12.8; Br, 31.12.) and the corresponding sulfone, mp 121–123°.

2,5-Bis(*p*-bromophenylthio)furan. 2,5-Bis(chloromercury)furan[8] (14.7 g) was suspended in dry chloroform (500 ml) and 4-bromosulfenyl chloride[9] (17.8 g) in chloroform (50 ml) was added under vigorous stirring. The mixture was refluxed for 20 min and then washed with water. The dry organic layer was concentrated and the residue was purified by column chromatography on silica gel; 5.0 g of the product, mp 89–90°, was obtained. Anal. Calcd for $C_{16}H_{10}Br_2OS_2$: C, 43.45; H, 2.28; S, 14.5; Br, 36.12. Found: C, 43.5; H, 2.3; S, 14.1; Br, 36.0.

2,3-Bis(*p*-bromophenylthio)furan. A mixture of 3,4-dibromo-2-furoic acid[10] (3 g), copper *p*-bromothiophenate[11] (6.27 g), chinoline (60 ml), and pyridine (5 ml) was stirred at 200–210° for 3 hr. The mixture, originally yellow-orange, turns green, then becomes homogeneous.

To the cooled solution was then added 10% hydrochloric acid (300 ml) and the mixture was extracted with benzene.

Chromatography on silica gel of the concentrated organic layer gave 0.8 g of an oil (Anal. Calcd for $C_{16}H_{10}Br_2OS_2$: C, 43.15; H, 2.28; S, 14.5; Br, 36.08. Found: C, 43.8; H, 2.3; S, 14.5; Br, 36.4.) which was directly oxidized with H_2O_2 in acetic acid to the corresponding disulfone, mp 182–184°. Anal. Calcd for $C_{16}H_{10}Br_2O_5S_2$: C, 37.96; H, 1.99; Br, 31.57. Found: C, 38.0; H, 1.97; Br, 31.7.

Fenton Reaction. To a mixture of furan (70 ml), *p*-bromothiophenol (3.8 g), *tert*-butyl alcohol (40 ml), and water (15 ml) was slowly added an aqueous solution of $FeSO_4 \cdot 7H_2O$ (6.2 g) and concentrated H_2SO_4 (2.2 ml), then, under vigorous stirring, 5.1 ml of 30% H_2O_2 during 1 hr, the temperature of the reaction mixture being 5–10°. The reaction mixture was left overnight at room temperature, then extracted with ether. From the ethereal solution was removed the unreacted thiophenol (3 g) by washing with 10% NaOH.

The residue was chromatographed on silica gel. The following products were separated and identified by analysis and comparison of spectral data (ir, NMR) with those of authentic models: 4,4′-dibromodiphenyl disulfide (0.56 g), 2(*p*-bromophenylthio)furan (0.1 g), and 2,3-bis(*p*-bromophenylthio)furan (0.4 g). The latter product was oxidized to a sulfone, mp 182–184°, identical with that obtained in the previously described independent synthesis. No 2,5-bis(*p*-bromophenylthio)furan or 3-(*p*-bromophenylthio)furan were identified in the reaction products.

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Registry No.—I, 53906-92-6; I disulfone, 53906-93-7; II, 53906-94-8; II sulfone, 53906-95-9; III, 5335-84-2; furan, 110-00-9; *p*-bromophenylthio radical, 31053-90-4; 3-(*p*-bromophenylthio)furan, 53906-96-0; 3-(*p*-bromophenylsulfonyl)furan, 53906-97-1; 2,5-bis(*p*-bromophenylthio)furan, 53906-98-2.

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The Anionic Addition of Dimethylamine to Isoprene

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The alkali metal catalyzed anionic addition of amines and ammonia to olefins and conjugated dienes affords an excellent route to alkyl-substituted amine systems.[1–9] Yields as high as 76% have been reported with various amines and olefins using lithium, sodium, or potassium metal or their corresponding hydrides.[6,9] Butyllithium has been employed to form the lithium amide intermediate, which readily adds to both vinyl aromatics and conjugated dienes.[1] The use of sodium metal for the addition of amines to conjugated dienes has been studied extensively. In fact, the sodium-catalyzed addition of dimethylamine to isoprene was originally reported to give 95% *N,N*,3-trimethyl-2-butenylamine (1) and 3% of an enamine.[4] However, subsequent investigations have shown that the formation of *N,N*,2-trimethyl-2-butenylamine (2) and 4% of an unidentified material, presumably **3**, also occurred.[10,11] Since the

$$(CH_3)_2NH + CH_2{=}C(CH_3){-}CH{=}CH_2 \longrightarrow$$

$$\underset{\mathbf{1}}{(CH_3)_2NCH_2CH{=}C(CH_3)_2} + \underset{\mathbf{2}}{(CH_3)_2NCH_2C(CH_3){=}CHCH_3} + \underset{\mathbf{3}}{(CH_3)_2NCH{=}CHCH(CH_3)_2}$$

base-catalyzed rearrangement of allyl amines to enamines is known,[12,13] the formation of **3** under these conditions is not unlikely. In fact, the presence of **3** in the reaction mixture has been confirmed by the isolation of the 2,4-dinitrophenylhydrazone of isovaleraldehyde from the acid hydrolysis of the reaction mixture and the sodium-catalyzed rearrangement of **1** to **3** has been studied.[13] This anionic addition presented an interesting problem in the possible control of the ratio of 1,4-addition product to 4,1-addition products, which are formed during the reaction, by changing the alkali metal catalyst used.

The sodium-catalyzed addition of dimethylamine to isoprene was conducted and gave three product peaks when