References and Notes

(1) For a review, see R. H. DeWolfe, "Carboxylic Ortho Acid Derivatives," Academic Press, New York, N.Y., 1970, p 348.

(2) M. Hojo and R. Masuda, unpublished work. Presented in part at the 27th Annual Meeting of the Chemical Society of Japan, Oct 12, 1972, Abstracts, III, p 365.

(3) H. Boehme and J. Roehr [*Justus Liebigs Ann. Chem.*, **648**, 21 (1961)] reported a reaction of triethyl trithioorthoacetate with acetyl chloride to form ketene diethyl dithioacetal and thiolacetate. In our experiment with $(ArS)_3CCH_3$ and acetyl chloride, no reaction occurred. However, if a small amount of acetic acid was present, resinous materials were produced, probably derived from the ketene dithioacetal.

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Homobenzylic and Homoallylic Spin-Spin Coupling Interactions in Some Octahydro- and Hexahydrophenanthridines

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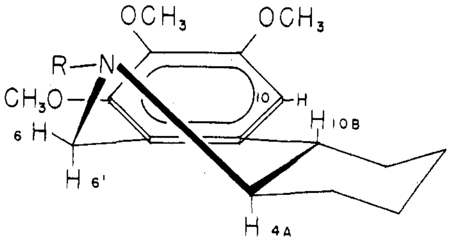
In a previous communication[1] we reported that the signals assigned to H-6′ in the NMR spectra of 1 showed splittings of ca. 1.5 Hz in addition to those expected from geminal coupling between H-6 and H-6′. The conformation of 1 is believed to be that shown here and was derived[1] mainly from nmr data. It can be seen that the protons most likely to be responsible for the additional splitting are H-10 (benzylic coupling),[2] H-4a (coupling across four single bonds),[2] or H-10b (homobenzylic coupling).[2] The original suggestion[1] of long-range coupling between H-6′ and H-4a would represent an unusual case of substantial coupling across four single bonds in non-W configuration.[2] An earlier report proposing such a case[3] has been shown to be incorrect.[4]



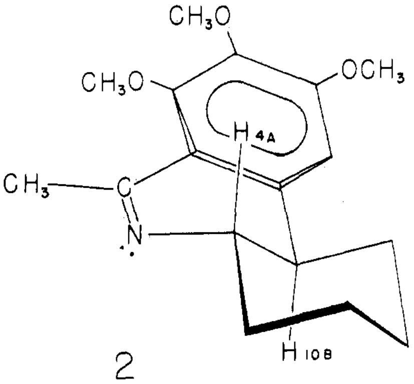
1 a R = Me

b R = Et

We now present conclusive evidence from 100-MHz multiple resonance studies and from studies on the 4a-deuterio derivative of **1a** that the observed interaction results from homobenzylic coupling between H-6′ and H-10b. The spectra of 1 have been reexamined in $CDCl_3$ at 100 MHz[5] by the Sydney group and, with the aid of multiple resonance experiments, it was established that the proton responsible for the long-range interaction with H-6′ (multiplet, δ 2.52 in **1a**) also interacts with H-10 ($J \simeq 0.8$ Hz, benzylic coupling).[2] Clearly, the resonance at δ 2.52 must be due to H-10b and the long-range interaction responsible for the additional splitting of the signals due to H-6′ is a homobenzylic coupling.[2] An analogous series of results was also obtained for **1b**. A careful measurement of the splittings in the signals due to H-6′, while the residual broadening due to interaction with H-10 was removed by decoupling, showed $J_{6',10b} = 1.88 \pm 0.03$ Hz in **1a** and 1.69 ± 0.03 Hz in **1b**, the largest homobenzylic interactions reported so far.[2,6] The assignment is confirmed by the spectrum of 5-methyl-7,8,9-trimethoxy-4a,10b-*trans*-1,2,3,4,4a,5,6,10b-octahydrophenanthridine-*4a-d*, in which the signal of H-6′ has the same multiplicity as seen with the undeuterated **1a.**

It is significant that these interactions and the similar, slightly smaller, spin-spin coupling in some sterically analogous steroids with ring A aromatic[4] are between trans disposed pseudo-axial protons, which is a particularly favorable juxtaposition for cisoid homoallylic coupling,[7] a related long-range spin-spin interaction.

In a previous communication[8] we have also reported homoallylic coupling constants of about 2 Hz between H-4a and the C-6 methyl protons in 6-methyl-7,8,9-trimethoxy-4a,10b-*trans*- (**2**) and -4a,10b-*cis*-1,2,3,4,4a,10b-hexahydrophenanthridine (**3**). These two compounds represent examples of transoid homoallylic coupling where a methyl group assumes the equilibrium conformation in systems where one sp^2 carbon is replaced by an sp^2-hybridized nitrogen atom. In view of the conformational dependence of homoallylic coupling constants,[7] the similarity of the observed homoallylic coupling constants in the trans and cis isomers indicates that H-4a must have essentially the same conformational relationship to the double bond in the two isomers, that is, one in which the dihedral angle between H-4a and the plane of the double bond approaches 90°. This requires that the predominant solution conformation of the cis isomer **3** be that in which the cyclohexane ring has the chair conformation with H-4a in equatorial and H-10b in axial orientations, contrary to what was previously proposed[8] on the basis of chemical shift arguments. The 100-



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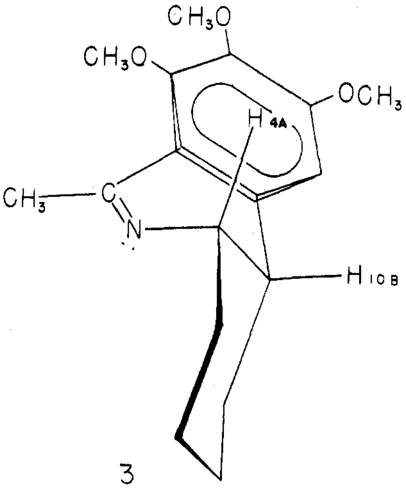

3

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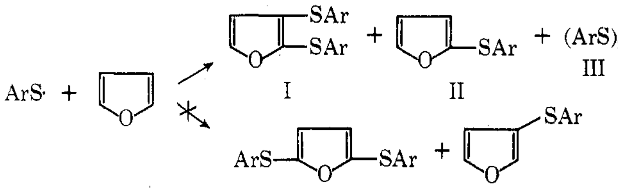
It is well known that furan can react with ionic[1] or radical[2] reagents, giving both substitution and 2,5-addition products; we wish now to report a case in which a 2,3-addition to the furan ring can explain the reaction products.

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

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

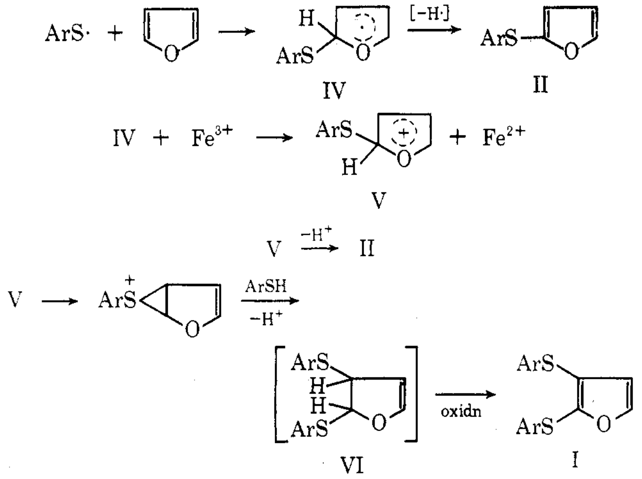
$$ArSH + \cdot OH \longrightarrow ArS\cdot + H_2O$$



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

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