

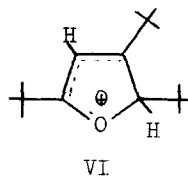
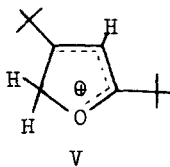
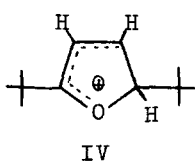
STABLE FURANONIUM IONS

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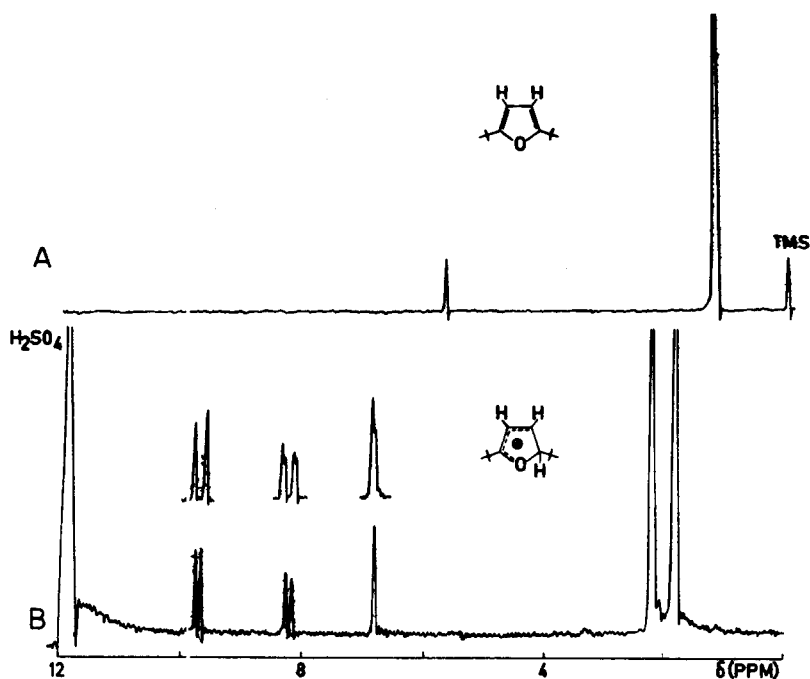
It appears that the *t*-butyl group confers unique stabilizing properties on certain heteroaromatic systems. Thus 2,5-di-*t*-butylfuran<sup>1</sup> (I), its 2,4-isomer<sup>2</sup> (II) and 2,3,5-tri-*t*-butylfuran<sup>1</sup> (III) dissolved in concentrated sulfuric acid show NMR spectra at a temperature of 38° which are in accord with the structures of respectively the species IV, V and VI.



For example the unprotonated furan I (spectrum A)<sup>3</sup> clearly shows one singlet due to two equivalent *t*-butyl groups and one singlet for the two equivalent ring protons. After protonation in 96% sulfuric acid (spectrum B)<sup>4</sup> two distinctly different *t*-butyl signals are observed at  $\delta$  1.74 and 2.13. The 2-proton absorbs at  $\delta$  6.73 and the dissimilar 3- and 4-protons give two doublets at  $\delta$  8.08 and  $\delta$  9.62 respectively.<sup>5</sup> (see figure).

The sulfuric acid solutions are completely stable for at least 10 days at room temperature. After hydrolysis of these solutions, the furans I<sup>8</sup>, II and III were recovered. No sulfonated products were found. These spectra are consistent with exclusive  $\alpha$ -protonation. This is in agreement with the proposed first step in the acid catalyzed ring opening of furans which has been studied in this laboratory earlier.<sup>9</sup> Experiments in dideuterosulfuric acid and in deuterotrifluoroacetic acid however indicate additional smooth exchange of the protons in the  $\beta$ -positions.

FIG.

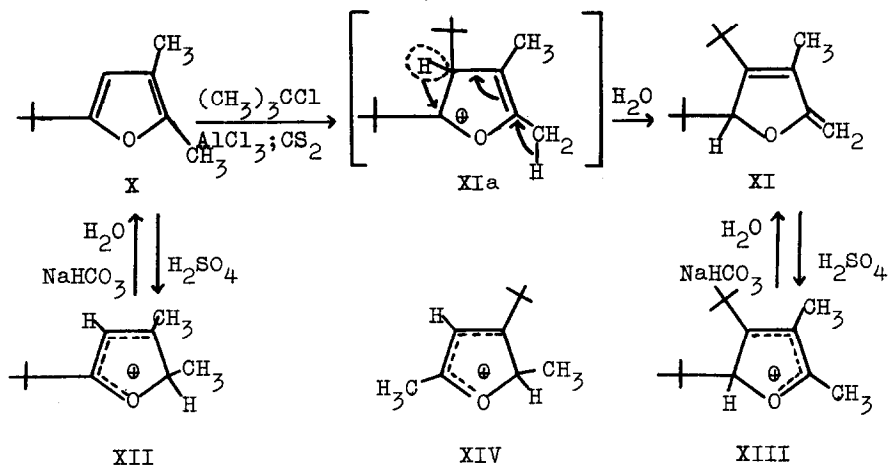


NMR spectra (see text)

2,4-Di-*t*-butylfuran (II) is protonated in the 5-position, and not in the 2-position. 2,3,5-Tri-*t*-butylfuran (III) is found to be protonated exclusively in the 2-position. The latter is best rationalized by considering the relief of strain when the two *ortho* *t*-butyl groups become non-planar. The chemical shifts and coupling constants are summarized in the table.

Undoubtedly as a consequence of the large steric requirements of a *t*-butyl group, the *t*-butylfurans resist resinification in sulfuric acid in contrast with other alkylfurans.<sup>10</sup> For the same reason *t*-butylfurans permit Friedel-Crafts alkylation in high yields.<sup>1</sup> Of interest is the *t*-butylation of 2,3-dimethyl-5-*t*-butylfuran<sup>11</sup> (X) with *t*-butylchloride in carbon disulfide using aluminum chloride as a catalyst. The reaction product was found to be 2-methylene-3-methyl-4,5-di-*t*-butyl-2,5-dihydrofuran (XI).

Although a formal rationalization via the electrophilic substitution transition state (XIa) followed by a hydride shift can be given, further studies are needed to accurately define the complex of reactions involved.<sup>12</sup>



The structure of XI, an unstable colourless oil, is supported by elementary analysis, molecular weight determination and the spectra. Moreover the structure is confirmed by the NMR spectrum of its sulfuric acid solution. 2-Methylene-3-methyl-4,5-di-t-butyl-2,5-dihydrofuran (XI) becomes protonated on the exocyclic double bond and the species XIII is formed. This is actually the furanonium ion derived from the hypothetical 2,3-dimethyl-4,5-di-t-butylfuran (XIb) by protonation in the 5-position. In this ion the t-butyl groups are out of the ring plane. Upon hydrolysis of the sulfuric acid solution the exocyclic conjugated diene system XI is recovered instead of the aromatic system XIb. Steric repulsion is obviously responsible for the fact that the tautomer XI is the more stable compound.

As indicated in the reaction scheme protonation of 2,3-dimethyl-5-t-butylfuran (X) and 2,5-dimethyl-3-t-butylfuran<sup>11</sup> (XV) with sulfuric acid, results in the formation of the ions XII and XIV respectively. The chemical shifts and coupling constants of XII, XIII and XIV are given in the table. In XIII and XIV we observed long range coupling between  $\text{CH}_2(2)$  and  $\text{H}(5)$  and between  $\text{H}(2)$  and  $\text{CH}_3(5)$  respectively.

TABLE

Chemical shifts <sup>⊠</sup> (in $\delta$ ) and coupling constants of protonated furans									
	H (2)	H (3)	H (4)	H (5)	CH <sub>3</sub> (2)	CH <sub>3</sub> (3)	CH <sub>3</sub> (5)	t-Bu <sup>⊠⊠</sup>	
IV	6.73 <sup>a</sup>	8.08 <sup>b</sup>	9.62 <sup>c</sup>					1.74; 2.13	a) doublet, $J_{2,3} = 1.2$ cps b) two doublets, $J_{3,4} = 6.0$ cps and $J_{2,3} = 1.2$ cps
V		7.79		6.62 <sup>d</sup>				1.96; 2.07	c) doublet, $J_{3,4} = 6.0$ cps d) two protons e) quadruplet, $J_{H(2)-CH_3(2)} = 7.5$ cps f) doublet, $J_{H(2)-CH_3(2)} = 7.5$ cps
VI	6.48	7.77	7.77					1.72; 1.96; 2.00	g) broadened peaks, $J_{H(5)-CH_3(2)} = 0.9$ cps
XII	6.59 <sup>e</sup>		7.63		2.25 <sup>f</sup>	3.07		1.96	h) multiplet i) doublet, $J_{H(2)-CH_3(2)} = 7.4$ cps
XIII				7.69 <sup>g</sup>	3.18 <sup>g</sup>	2.33		1.67; 2.06	j) doublet, $J_{H(2)-CH_3(5)} = 2.9$ cps
XIV	6.78 <sup>h</sup>		7.66		2.45 <sup>i</sup>		3.49 <sup>j</sup>	1.95	

<sup>⊠</sup> The NMR spectra were taken on a Varian A-60 using tetramethylsilane in trifluoroacetic acid as an external standard ( $\delta_{TMS} = 0$ ).

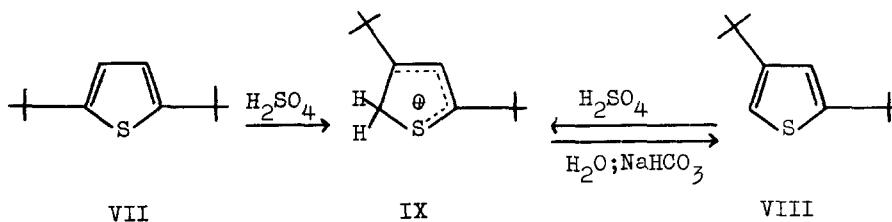
<sup>⊠⊠</sup> The t-butyl groups cannot be assigned unambiguously.

Comparable NMR spectra of protonated pyrrole derivatives are known<sup>13</sup> and recently in low temperature NMR spectra of protonated methylthiophenes a similar coupling was reported.<sup>14</sup>

It must be noted that even a t-butyl group in the 3-position, as in XV, has a pronounced stabilizing effect. Thus in contrast to the rapid decomposition of 2,5-dimethylfuran in sulfuric acid 2,3-dimethyl-5-t-butylfuran (X) and 2,5-dimethyl-3-t-butylfuran (XV) were recovered unchanged from their sulfuric acid solutions.

## REFERENCES.

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2. J.A. Miller, M.H. Durand and J.E. Dubois, Tetrahedron Letters, 1965, 2831.
3. In carbon tetrachloride using tetramethylsilane (TMS) as internal standard ( $\delta_{\text{TMS}} = 0$ ).
4. Tetramethylsilane in trifluoroacetic acid as external standard ( $\delta_{\text{TMS}} = 0$ ).
5. We have obtained a similar spectrum upon dissolution of 2,5-di-t-butylpyrrole<sup>6</sup> in sulfuric acid. When 2,5-di-t-butylthiophene<sup>7</sup> (VII) was dissolved in sulfuric acid, it was completely converted into the protonated form (IX) of its 2,4-isomer<sup>7</sup> (VIII):



This reaction is of synthetic value since in the direct t-butylation of thiophene a mixture of VII and VIII is obtained.<sup>7</sup> Treatment of this mixture with sulfuric acid for 6 hours gives the pure 2,4-isomer (VIII) in almost quantitative yield.

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9. E.J. Stambuis, W. Drenth and H. van den Berg, Rec.Trav.Chim., 83, 167 (1964).
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11. Correct analytical data were obtained for all new compounds reported.
12. We have observed a similar behaviour in a number of additional t-butyl-alkylfurans.
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Y. Chiang and E.B. Whipple ibid. 85, 2763 (1963).
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