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FURANO[3,4-*d*]THIEPIN: A NON-CLASSICAL HETEROAROMATIC SYSTEM

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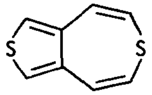
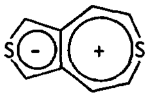
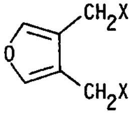
The synthesis of a stable thiepin, thieno[3,4-*d*]thiepin (I), has been reported recently.[1] Chemical, spectroscopic, and X-ray examination of I show this $4n$-π-electron heterocycle to be an extensively delocalized aromatic system in which the azulene-like charge-separated species II contributes significantly to the ground state.[2] The remarkable properties found for I prompted us to study the effects that electrical asymmetry might have on the thermal stability and chemical reactivity of *d*-annulated thiepins. In this regard, we have prepared an oxygen analogue of I, furano[3,4-*d*]thiepin (III).


I

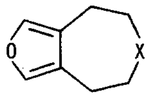

II


III

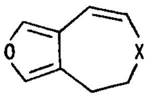
Lithium aluminum hydride reduction of the furan diacid IV [3] gave rise to diol V which on treatment with a mixture of triphenylphosphine and carbon tetrachloride in dimethylformamide solution afforded the dichloride VI in good overall yield.[4] Reaction of VI with sodium sulfide in refluxing alcohol gave the tetrahydrothiepin VII (90%).[5] Conversion of VII into the corresponding sulfoxide VIII followed by dehydration of VIII with acetic anhydride gave in modest overall yield the dihydrothiepin IX. This product was in turn converted into the sulfoxide X (80%) by carefully controlled oxidation with *m*-chloroperbenzoic acid. When sulfoxide X was reacted with acetic anhydride at 150° for 30 minutes under light-shielded and rigorously degassed conditions, thiepin III was formed as a lemon yellow solid mp 116° in 22% yield. In addition, both the thiepin sulfoxide XI and thiepin sulfone XII have been prepared by oxidation of III with *m*-chloroperbenzoic acid.



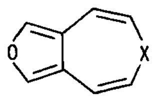
IV, X = CO_2H
V, X = CH_2OH
VI, X = CH_2Cl



VII, X = S
VIII, X = SO



IX, X = S
X, X = SO

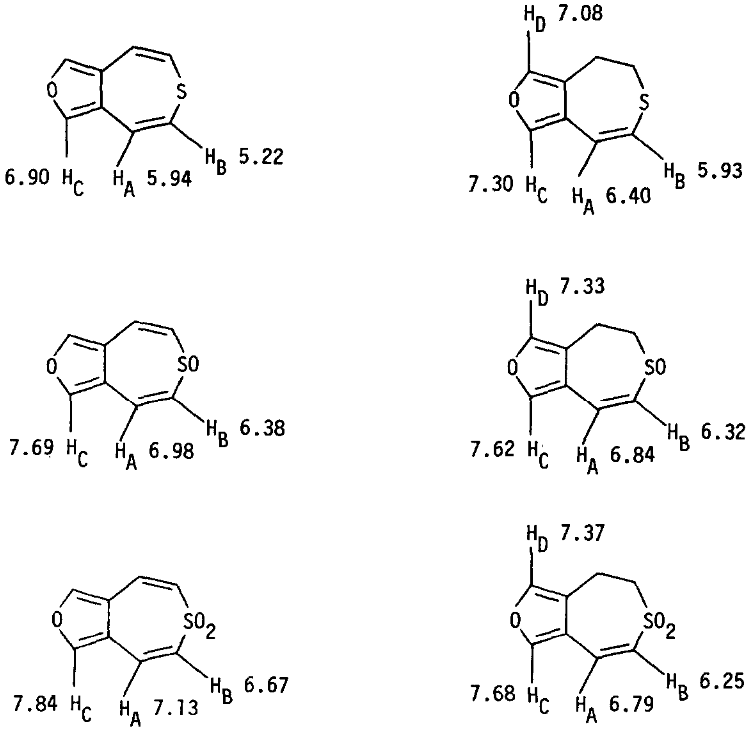


XI, X = SO
XII, X = SO_2

The spectroscopic behavior of III, XI, and XII corresponds to that observed for thiepin I and its S-oxide analogues. Heterocycle III shows extended conjugation with ultraviolet and visible absorption maxima at $\lambda_{max}^{CH_3OH}$ 225 nm (ε = 15,700), 233 (17,440), 240 (26,610), 249 (23,900), 275 (1,121), 345 (468), 364 (514), and 415 (140). Sulfoxide XI showed only ultraviolet absorption at $\lambda_{max}^{CH_3OH}$ 225 nm (ε = 15,211) and 270 (4,016) while sulfone XII gave absorption at $\lambda_{max}^{CH_3OH}$ 229 nm (ε = 25,600) and 270 (2,770). In addition, the nmr values found for III show a pronounced upfield shift when compared to the vinyl sulfide IX; the same phenomenon also was observed for thiepin I.[2] Figure I shows the chemical shifts (values given in δ) for thiepins III, XI, and XII along with their corresponding dihydro analogues.

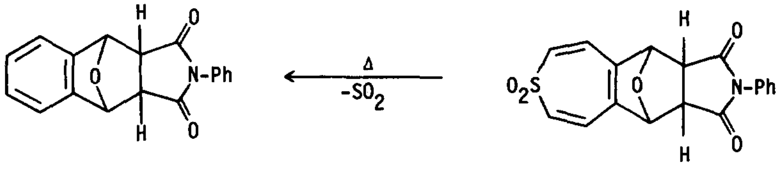
Not surprisingly, the reactivity of the furanothiepins towards dienophiles is much greater than that found for the thienothiepins.[2] Thus, thiepin III and its sulfoxide derivative XI on reaction with N-phenylmaleimide at 25° gave rise (90% yield) to a 3:2 mixture of the *exo* and

Figure 1



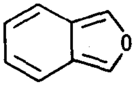
endo adducts XIII and XIV respectively. These same adducts in a different ratio were also obtained from isobenzofuran XV [6] and N-phenylmaleimide. In marked contrast, reaction of the furanothiepin sulfone with N-phenylmaleimide at 25° occurred without loss of sulfur dioxide, and a mixture of the thiepin sulfone adducts XVI and XVII was formed. The infrared, ultraviolet, and mass spectrum of XVI and XVII are in agreement with their assigned structure.[7] In addition, heating these adducts above 100° resulted in the formation of adducts XIII and XIV accompanied by the loss of sulfur dioxide.[8]

At temperatures as low as -65°, the furanothiepins III and XI were observed to rapidly react with the dienophile but, intermediate thiepin or thiepin sulfoxide adducts could not be chromatographically or spectroscopically detected. However, the great reactivity of these annulated thiepins does suggest that appropriately substituted derivatives of III might be used to prepare stable non-annulated 8-π-electron thiepins by this novel Diels-Alder route.



XIII and XIV

XVI and XVII



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3. K. Y. Norilskii, Y. K. Yurev, V. N. Zhingareua, and K. Gresl, *Zhur. Obs. Khim.*, **34**, 2568 (1964).
4. A. W. Friederang and D. S. Tarbell, *J. Org. Chem.*, **33**, 3797 (1968).
5. Satisfactory spectral and analytical data were obtained on all new compounds.
6. L. F. Fieser and M. J. Haddadin, *Can. J. Chem.*, **43**, 1599 (1965), and references cited therein.
7. The insolubility of XVI and XVII precluded obtaining good nmr spectra of these adducts. However, the other spectral data for these adducts were in good agreement with the properties reported by W. L. Mock, *J. Amer. Chem. Soc.*, **89**, 1821 (1967) for the parent thiepin sulfone.
8. Thermal loss of sulfur dioxide also occurs from the parent thiepin sulfone (reference 9).