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REACTIVE AROMATIC HETEROCYCLES CONTAINING TETRAVALENT SULFUR. II.[1]

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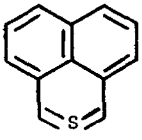
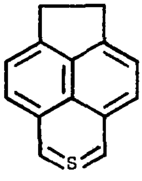
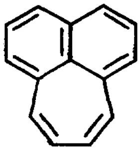
Recently we have shown that appropriately substituted cyclic sulfoxides when subjected to the Pummerer reaction undergo loss of the elements of water to form highly reactive heterocyclic species containing tetravalent sulfur.[1,2] Thus, naphtho[1,8-cd]thiapyran (I) and acenaphtho-[5,6-cd]thiapyran (II), isoelectronic analogues of the aromatic hydrocarbons peri-cycloheptanaphthalene (III)[3] and peri-cycloheptaacenaphthene (IV),[3] have been generated in good yield from their corresponding sulfoxides.



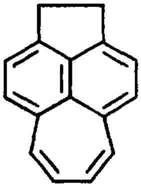
I



II

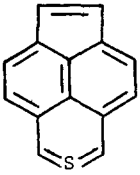


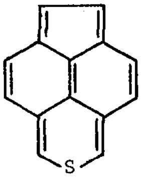
III

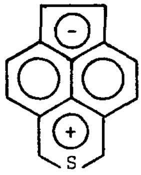


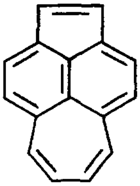
IV

In an effort to gain further insight into the novel sulfur bonding found in systems I and II, it was decided to attempt the preparation of a third heterocyclic member of this series, acenaphthyl[5,6-cd]thiapyran (V), a tetracovalent sulfur analogue of the extremely stable aromatic hydrocarbon peri-cycloheptaacenaphthylene (VI).[3] Heterocycle V was of particular interest in that it contains $4n+2$ peripheral π electrons while compounds I and II do not. Additionally, V may be written in a quinonoid resonance form containing divalent sulfur (Va) as well as in a charge separated form (Vb). Such contributors are not possible for heterocycles I and II. Enhanced aromatic character and a possible difference in the Diels-Alder behavior therefore seemed reasonable expectations for the chemistry of V. We wish to describe now the generation of V and in addition to report a novel sulfoxide rearrangement encountered during the course of this work.


V


Va

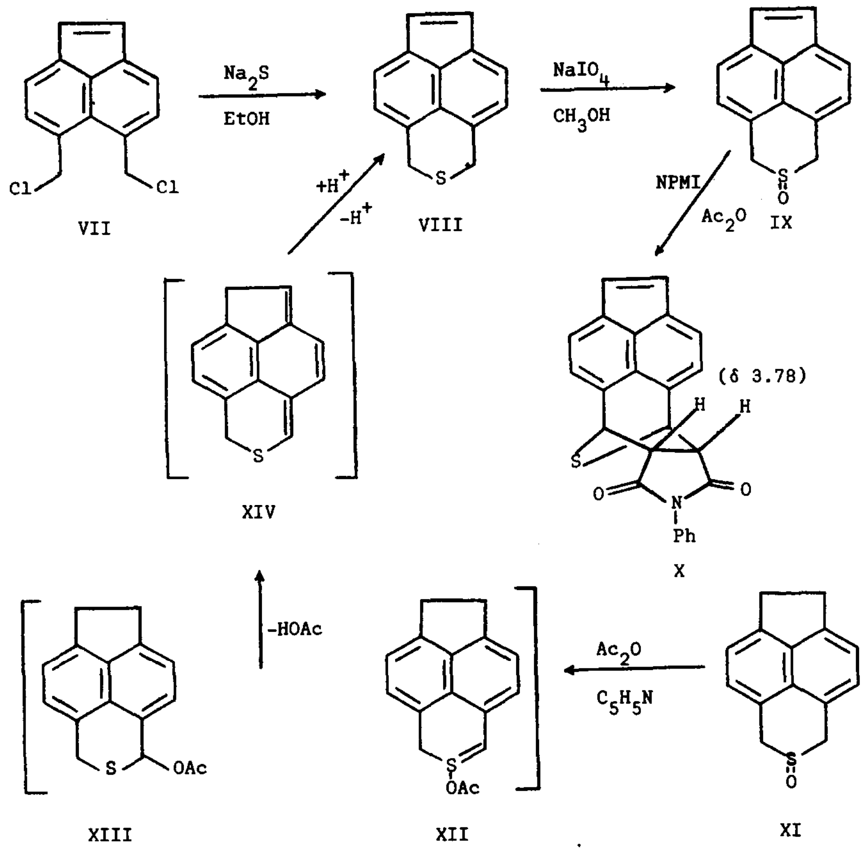

Vb


VI

Treatment of 5,6-bis(chloromethyl)acenaphthylene (VII)[4] with either phosphorus pentasulfide in carbon disulfide or anhydrous sodium sulfide in ethanol gave in 95% yield sulfide VIII, mp. 172°.[5] The structure of VIII was provided by its mass spectrum (parent ion a 210) and by its nmr spectrum which shows two vinyl protons at δ 6.90 in addition to four protons α to the sulfide group at δ 4.07 and a well resolved multiplet of four aromatic protons in the δ 7.15-7.50 region.[6] Oxidation of VIII using sodium periodate in aqueous methanol[7] afforded the corresponding sulfoxide IX, mp. 236° dec., in 90% yield. The infrared spectrum of IX showed a band at 1040 cm^{-1}, characteristic of sulfoxides, while its nmr spectrum exhibited four protons α to the sulfoxide group at δ 4.42 as well as two vinyl protons at δ 7.00 and the usual multiplet of aromatic protons at δ 7.30-7.75.

Reaction of IX in refluxing acetic anhydride was found to occur readily accompanied by the formation of a complicated mixture of products. However, decomposition of the sulfoxide with acetic anhydride in the presence of N-phenylmaleimide proceeded smoothly giving rise in 60% yield to a single crystalline adduct X, mp. 273° dec. The *exo* configuration was assigned to X on the basis of its nmr spectrum which shows the two protons α to the imide carbonyls at δ 3.78, a position very similar to that (3.75) of the corresponding protons of the N-phenylmaleimide adducts of heterocycles I and II.[1]

The considerable reactivity observed for heterocycle V along with its behavior in the Diels-Alder reaction would seem to indicate that it is best viewed as a tetracovalent sulfur species with π electron delocalization comparable to compounds I and II.



The conversion of sulfoxides to α-acetoxy sulfides has long been considered to proceed through S-acetoxy ylide intermediates.[8] It seems reasonable to assume a similar mechanism involving subsequent 1,2 or 1,3 elimination of acetic acid from either an S-acetoxy ylide or an α-acetoxy sulfide intermediate occurs in the formation of the heterocycles described here. The acenaphthene derived sulfoxide XI[1] offers an additional and intriguing possible transformation since vinylogous elimination of acetic acid from the ylide XII or the acetate XIII followed by protropic rearrangement of the resulting quinonoid intermediate XIV could give rise to the acenaphthylene sulfide VIII. Some credence for this possibility is found in the previously reported dehydration of 5-(α-hydroxybenzyl)acenaphthene to 5-benzylacenaphthylene.[9] A quinonoid intermediate similar to XIV was proposed for this reaction.

The occurrence of sulfide VIII however, could not be detected on decomposition of sulfoxide XI with refluxing acetic anhydride, conditions under which VIII was found to be stable.[10] In marked contrast to this result, reaction of XI with acetic anhydride in the presence of added base (sodium acetate, triethylamine or pyridine) gave sulfide VIII in 30% yield along with heterocycle II (isolated as a Diels-Alder adduct). Numerous attempts to improve the yield of this reaction by employing a variety of bases and anhydrides has met thus far with limited success.

Application of the reactions described here to the synthesis of a number of unusual sulfur heterocycles is in progress and will be reported at a later date.

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2. Additional examples of this reaction have been observed by M. P. Cava and N. M. Pollack, J. Am. Chem. Soc., 89, 3640 (1967).
3. (a) V. Boekelheide, W. E. Langeland and C. Liu, J. Am. Chem. Soc., 73, 2432 (1951).
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4. L. A. Carpino and S. Gowecke, J. Org. Chem., 29, 2824 (1964).
5. Elemental analyses of all new compounds are in accord with the assigned structures.
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10. The conditions described here for the decomposition of sulfoxide XI results in the high yield formation of heterocycle II. It therefore seems reasonable to conclude II is not a precursor of sulfide VIII.