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UNUSUAL CHEMICAL BEHAVIOR OF 1,2-DITHIAACENAPHTHENE IN THE REACTIONS WITH DINITROGEN TETRAOXIDE AND AQUEOUS BROMINE —— IN CONTRAST TO THE ORDINARY OXIDATION WITH FENTON REAGENT

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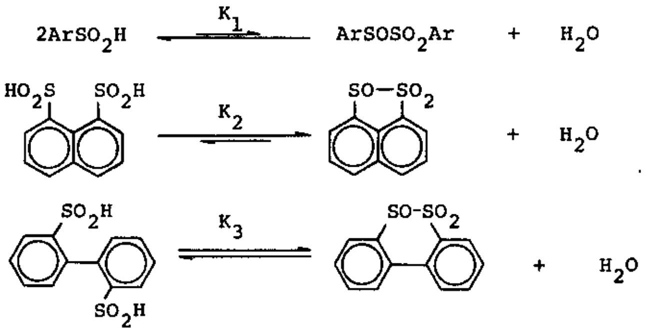
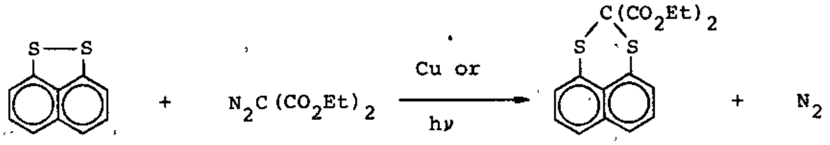
Abstract —— Unlike open chain disulfides or even cyclic disulfides, which are readily oxidized by N_2O_4 and aqueous bromine to sulfinyl and/or sulfonyl derivatives, 1,2-dithiaacenaphthene is readily nitrated with N_2O_4 and brominated with aqueous bromine at the naphthalene ring. Other oxidants, such as Fenton system: H_2O_2-$TiCl_3$, gave predominantly 1,2-dithiaacenaphthene 1-oxide as in the oxidation with H_2O_2.

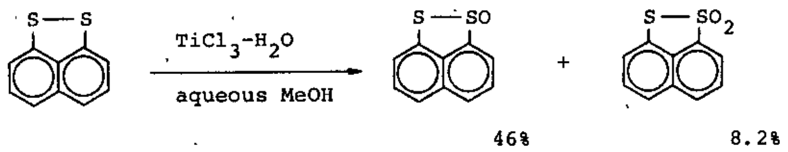
1,2-Dithiaacenaphthene is an interesting disulfide in that both sulfur atoms are confined rigidly at two peri-positions of naphthalene ring without ring strain, since the bond distance of the S-S linkage is considered to be nearly equal to that between the two peri-positions of naphthalene.[1,2] Yet the dihedral angle around the S-S linkage is nearly zero, which is very much apart from the average dihedral angle of the disulfidic linkage, i.e. 103°.[3] Therefore, due to the repulsion of lone electron pairs of the two divalent sulfur atoms, the S-S bond should be substantially energy-rich and hence would be highly reactive. Another unique feature of 1,2-dithiaacenaphthene is that the two sulfur atoms are rigidly confined in juxtaposition and cannot move away. Due to this situation,[4] neither nucleophilic nor homolytic substitution reaction on the sulfur atom would be favoured, while electrophilic reactions on the S-S bond such as oxidation and carbene insersion would take place quite readily. Although there has been no direct comparion of the rates of nucleophilic substitution of 1,2-dithiaacenaphthene with that of the analogous open chain disulfide, the alkaline hydrolysis of the monooxy derivative, i.e. 1,2-dithiaacenaphthene monooxide, is known to be 10^3 times slower than that of the open chain analogue, phenyl benzenethiolsulfinate,[1] while the equilibrium constants for ring opening of the dioxy derivative, 1,2-dithiaacenaphthene 1,1-dioxide, with both of CN^- and SO_3^{2-} ion are about 20 times smaller than those for the six-membered thiolsulfonates, biphenylene 2,2-disulfide-S-dioxide.[5] The most typical example to illustrate the cohesive effect may be found in the relative ratio of the three equilibrium constants,



$K_1 \ll K_3 \ll K_2$.[6-9] Meanwhile, the energy-rich S-S bond of 1,2-dithiaacenaphthene readily reacts with such an electrophile as diethyl diazomalonate to afford the carbene insersion product[10] and is also readily oxidized with $NaIO_4$ to the monooxide.[1]

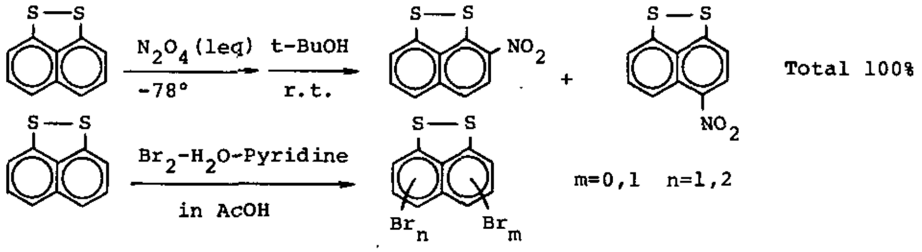


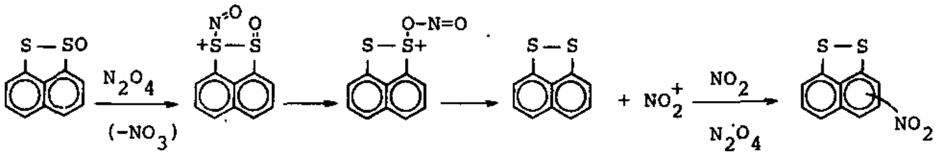
Therefore, the S-S bond is considered to be oxidized very readily by more electrophilic oxidants, such as N_2O_4, aqueous bromine and the Fenton reagent since the possible ring nitration, bromination and hydroxylation are rather incredible in view of the facile reaction of disulfide linkage of diphenyl disulfide with N_2O_4,[11] and the markedly larger reactivity of disulfide bond toward bromine and other electrophiles such as peroxy acids.[12-14] Indeed, the Fenton system, $TiCl_3$-H_2O_2 in aqueous methanol which generates hydroxy radical, was found to oxidize 1,2-dithiaacenaphthene mainly affording the monooxide together with a small amount of the dioxide. For example, when one equivalent of the disulfide was treated with two equivalents of $TiCl_3$ and 7 equivalents of H_2O_2 in five minutes at room temperature, the following result



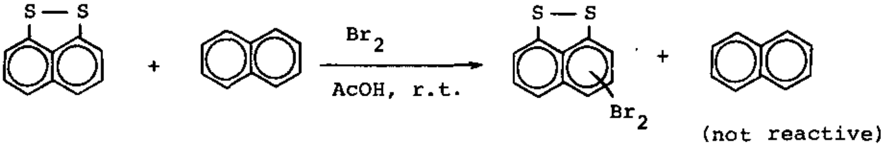
was observed. Similar results were observed in the oxidations of 1,2-dithiane, diphenyl disulfide and others.

However, contrary to our expectation, no S-oxygenation product was obtained in the treatment of 1,2-dithiaacenaphthene with either N_2O_4 in CCl_4 or bromine in H_2O-pyridine-AcOH mixture. Instead, electrophilic substitution took place on naphthalene ring of 1,2-dithiaacenaphthene. Although the possibility of the S-monooxide or the dioxide as an intermediate in the nitration may be ruled out since the monooxide reacted with N_2O_4 only at room temperature while 1,1-dioxide is quite inert to N_2O_4 at room temperature, it is interesting to note that treatment of the monooxide with one equivalent of N_2O_4 at room temperature also gave mainly ring-nitrated dithiaacenaphthene together with a small amount of the dioxide, recovering some of the monooxide. The formation of ring nitrated dithiaacenaphthene may be rationalized by the following mechanistic scheme.





Pedulle et al. reported[15] that the monobromo derivatives were obtained quantitatively in the treatment of 1,2-dithiaacenaphthene and the open-chain analogue, 1,8-dimethylthionaphthalene, with bromine with in carbon tetrachloride-acetic acid(3:1) at room temperature. In the presence of water, however, 1,8-dimethylthionaphthalene gave mainly the monooxide while only ring bromination took place with 1,2-dithiaacenaphthene. The reactivity of dithiaacenaphthene toward bromine is so high that when a 1:1 mixture of dithiaacenaphthene and naphthalene is treated with one equivalent of bromine, only 1,2-dithiaacenaphthene was brominated without touching naphthalene. The enormously large reactivity of the naphthalene ring of dithiaacenaphthene toward N_2O_4 or Br_2 clearly indicates that there is a strong interaction between the non-bonding p-orbitals of



the two sulfur atoms and the π-system of the naphthalene ring and the lone pairs of the two sulfur atoms are delocalized over the entire molecule as the earlier theoretical treatments,[16-19] UV spectra,[19-21] and others [15,16,19,20] have suggested. If each one lone pair of the two sulfur atoms of 1,2-dithiaacenaphthene participates in the electron-delocalization over the entire molecule, the whole molecule should gain π-aromaticity with 14 electrons.

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