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1H - PHENOTHIAZIN - 1 - ONES,
A NEW CLASS OF HETEROCYCLIC ORTHO-QUINONEIMINES

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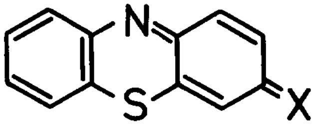
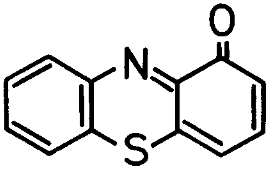
The p-quinonoid 3H-phenothiazin-3-one, (Ia), and its 3-imino analogues (Ib), hold an important place in the chemistry of phenothiazine;[1-3] on the opposite, o-quinonoid systems derived from this heterocycle are mentioned only as limiting structures of the cationic and radicalic oxidized species.[1,4]



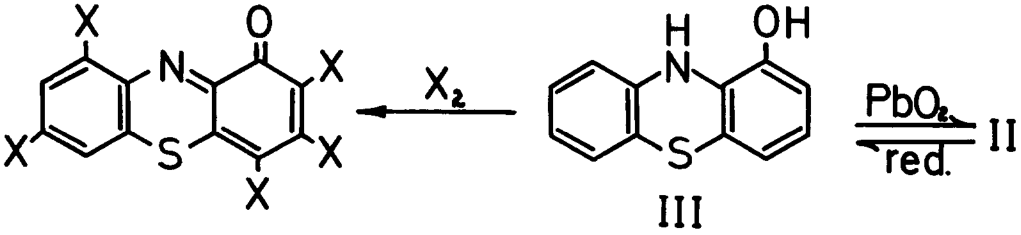
Ia, X=O; Ib, X=NR$_2^+$



II

We wish to report the synthesis and characterization of 1H-phenothiazin-1-ones, (II and IV), the first o-quinones in the phenothiazine series.

1-Hydroxyphenothiazine, (III), obtained either by treating 1-methoxyphenothiazine with pyridine·HCl[5] (or, with better yields, by the thionation of 2-hydroxydiphenylamine), was oxidized with PbO_2 (or AgO) in inert solvents, to yield dark-blue solutions of II. The quinone was obtained as dark blue-vi-



IVa, X=Br; IVb, X=Cl

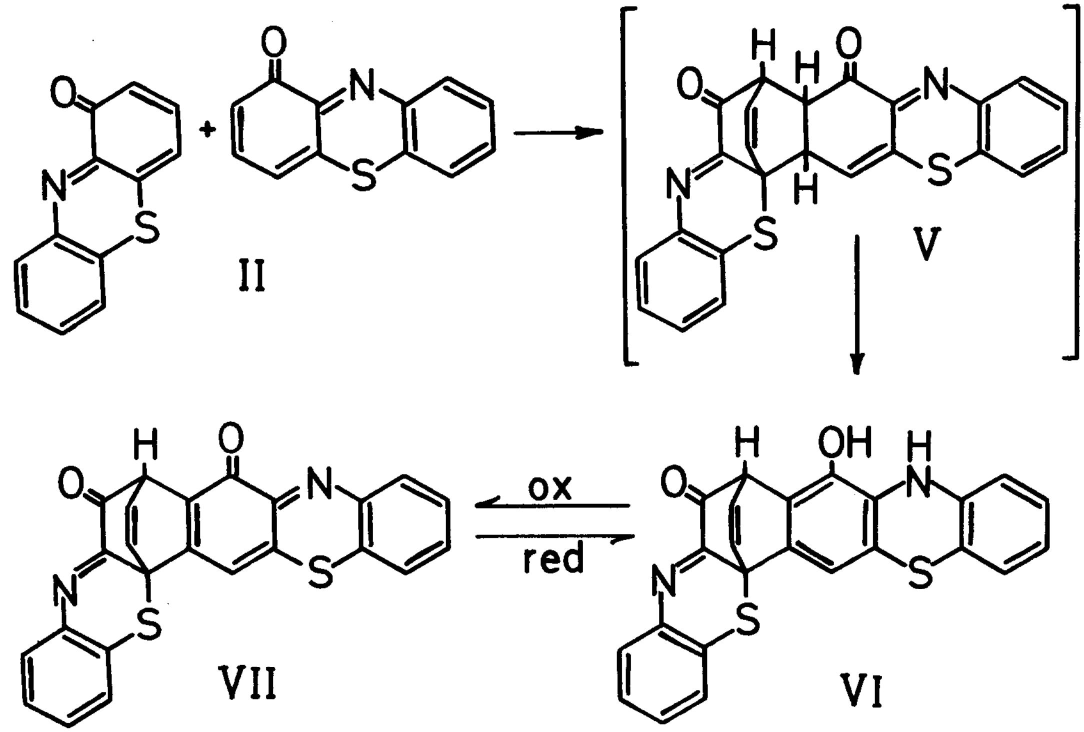
olet needles in almost quantitative yield by rapid evaporation of its diluted solutions. It melts at 110-11° when introduced in a preheated bath.

By treating III with Br_2 in boiling acetic acid, 2,3,4,7,9-pentabromo-1H-phenothiazin-1-one (IVa), m.p. 243° (preheated bath) was obtained in excellent yield; short time chlorinations of III in acetic acid gave the pentachloro derivative, (IVb), m. 243°, as the main product. In these reactions, the excess of halogen brought about the oxidations to quinones; on prolonged action, both Cl_2 and Br_2 induced the formation of crystalline addition products, now under investigation.

All II and IV are coloured in various shades of blue and green, mainly due to a characteristic band around 645 nm in their electronic spectra. As most Ia absorb at about 500 nm, it follows that the extending of the conjugated system resulted in a ~150 nm bathochromic shift, a value well within the range of the 120-160 nm shifts characteristic for o-p-quinone pairs of comparable backbones. The ν_{CO} vibrations give rise to a well marked band at 1642-1660 cm^{-1}, that is, at higher frequencies than in the spectra of the corresponding Ia.[6] Fission of C-X bonds and elimination of CO dominate the first fragmentations of the molecular ions in the mass spectra. The classical conversions of II and IV into 1-hydroxyphenothiazines by reducing agents (Zn/AcOH, $Na_2S_2O_4$) and back to the quinones by means of PbO_2, were also performed.

The dominant feature of the chemical behaviour of II consists of its propensity to dimerize. This process takes place even at room temperature, in the solid state, and is much accelerated by heat, thus preventing the determination of the melting point by the usual slow heating procedures. In concentrated solutions the dimerization is almost instantaneous; therefore, only diluted solutions and rapid evaporation can be used to isolate the quinone. The dimerization is coupled with secondary processes, the most important being the formation of III.

The very low solubility of the dimer renders its investigation by NMR difficult; however, the appearance of new signals in the region of vinylic protons could be observed by monitoring the dimerization in the resonance cavity. The pure dimer, black green crystals, m. >350°, was obtained by oxida-



tion of III with PbO_2 in concentrated solutions, followed by recrystallization from *o*-dichlorobenzene. The electronic spectra revealed the existence of a chromophore possessing the structure of II (identical λ_{max} and shape of the long-wave band), as well as the appearance of a new chromophore, absorbing at 480 nm. The occurence of quinonoid elements in the structure of the dimer is proved by reversible redox processes, as for the parent II. Moreover, dimer solutions in acetic acid, reduced with Zn, were lacking the long-wave band, whereas the band arising from the second chromophore was only slightly shifted.

Taking into account the existing data on the dimerization of *o*-quinones,[7-11] as well as the above mentioned physical and chemical properties of the dimer, we assume that the latter is formed as shown in the scheme. Thus, the initial Diels-Alder adduct, (V), not isolated so far, undergoes very rapidly the usual rearrangement to aromatic structures, yielding the quinol VI, which is immediately oxidized by PbO_2 to the final product, (VII). During the spontaneous dimerization of II, the latter oxidizes VI to VII, and is converted in its turn to III. This explains the formation of VII and III as the two major products of such dimerizations.

A 2+2 cycloaddition pathway, the only which would also account, at least partially, for the properties of VII, can be ruled out, since such a dimerization was not yet observed in thermal reactions,of *o*-quinones[7-11] and because irradiation of II in solutions rather retarded the formation of VII.

As expected, the halogenophenothiazones IV are much more stable against dimerization. However, IVa dimerizes on refluxing in *o*-dichlorobenzene or on heating in the solid state, whereas the chloro analogue, IVb, can be recrystallized from DMF and melted without dimerization. This difference is presumably decided in the rearomatization step (corresponding to V→VI), the one which makes the process irreversible; the required breaking of the C-X bonds occurs easier in the case of bromine. The analyses of the dimer of IVa showed the loss of one Br atom per phenothiazine moiety.[12]

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