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SOME REMARKABLE OXIDATIONS OF 2,3,5,6-TETRACHLORO-P-PHENYLENEDIAMINE, AND PRODUCTS THEREFROM

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Summary: The oxidation of 2,3,5,6-tetrachloro-p-phenylenediamine with Cl_2 or Br_2 in CCl_4 containing I_2 affords unusual quinoniminium salts displaying remarkable chemical behaviour.

THE exhaustive chlorination of aromatic amines can proceed violently. Even conducting it carefully, it usually affords complex mixtures of chlorination and oxidation products. However, such problems can be circumvened by performing consecutive, stepwise chlorinations.[1,2]

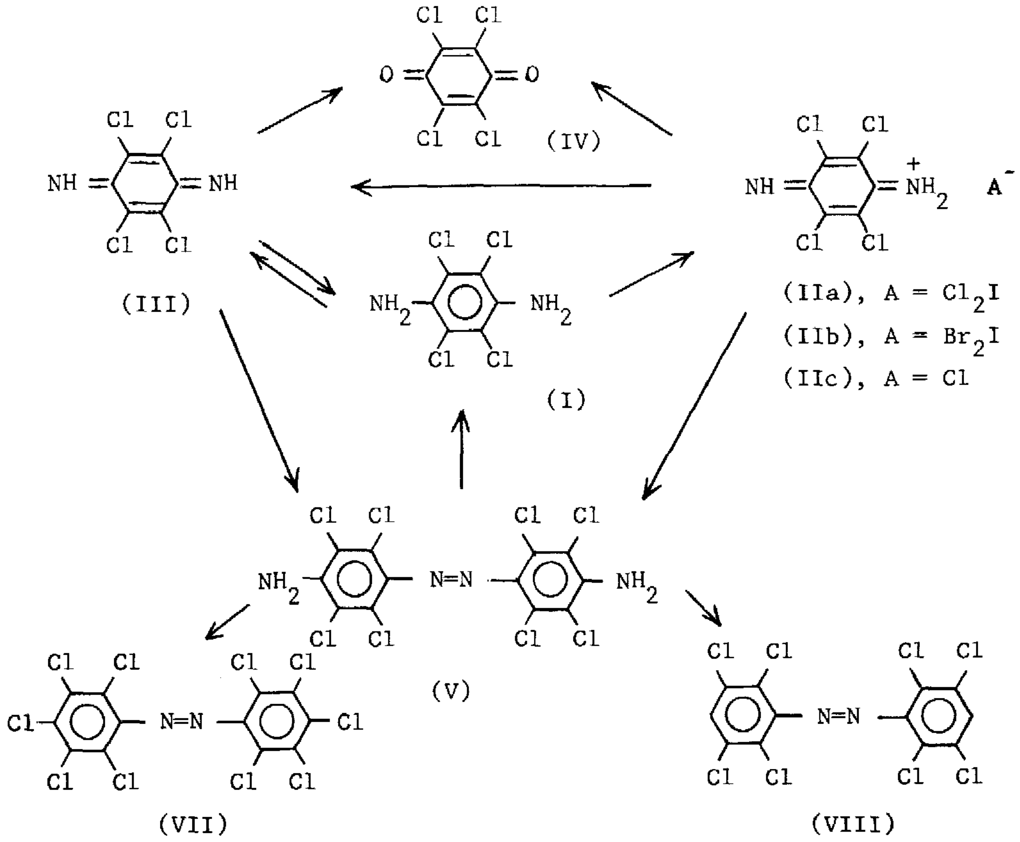
Therefore, taking this into account, and for the purpose of synthesizing octachloro-p-phenylenediamine, exhaustive chlorination of 2,3,5,6-tetrachloro-p-phenylenediamine (I) was undertaken. In previous work this was effected by means of $NaOCl/Cl_2$ giving however non-aromatic compounds.[3] Consequently, the chlorination of (I) with Cl_2/I_2 in CCl_4, at room temperature and in the dark, has been attempted. 2,3,5,6-Tetrachloro-p-quinon-4-imino-1-iminium dichloroiodide (IIa) (98.6%) separates immediately as a black infusible powder (dec. 150°). Analogously, (I) gives 2,3,5,6-tetrachloro-p-quinon-4-imino-1-iminium dibromoiodide (IIb) (99%) with Br_2/I_2. (IIa) and (IIb) analyze correctly for C, H, N, Cl, I, and Br. Their ir spectra are almost coincident and do not show any benzenoid absorption. Their uv-vis spectra are also almost coincident in the interval 260--550 nm; however, they differ appreciably in the region where anions ICl_2^-, and IBr_2^- absorb (200-260 nm).[4,5]

The name given above for (II) is based on the π-electron charge distribution. MNDO[6] SCF MO calculations on (II) show however that this cation is essentially a carbon ion, since there is no significant "total" positive charge on the nitrogen atoms.[7] Nevertheless, the π formal charge resides mostly on the nitrogen linked to carbon 1 (0.470) and on this carbon (0.297).

Salt (IIa), with aq. NaOH (or NH_3 in CCl_4), gives an excellent yield of 2,3,5,6-tetrachloro-p-quinondiimine (III); uv: λ (ε) (C_6H_{12}) 271 (22,500), 283 (29,900) and 310-325 (1250) nm. (III) has been synthesized independently by oxidation of (I) with $K_3Fe(CN)_6$/NaOH in benzene-water (95%), or with $KMnO_4/K_2CO_3$ in $CHCl_3$-water (80%), as reported.[8] (III) reverts to (I) with Zn/NaOH in refluxing methanol.

Quinondiimine (III) with anh. HCl in CCl_4 gives 2,3,5,6-tetrachloro-p-quinon-4-imine-1-iminium chloride (IIc) as a red solid which reverts easily to (III). Salts (IIa) and (IIc), as well as quinondiimine (III), hydrolize quantitatively to chloranil (IV) with water or with aq. HCl, respectively.

Solid black salts (IIa) and(IIb), when treated with cold anh. methanol, convert immediately into bright-red crystals of 4,4'-diaminooctachloroazobenzene (V) (77 and 84%, respectively), m.p. 339-42°; MS: m/e 843.79165; calcd. for

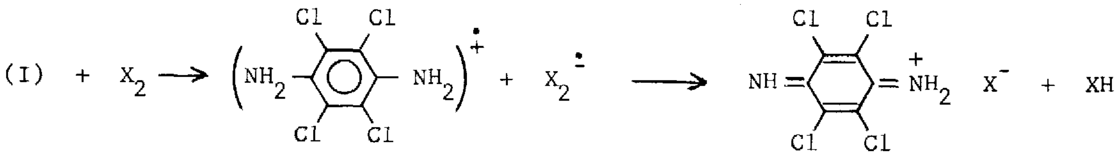


$C_{12}H_4N_4Cl_8^{35}$ 483.79443. (Similarly, salt (IIc) with methanol gives azobenzene (V); along with some (IV).) (V) analyzes correctly for C, H, N, and Cl.

Quinondimine (III) shows a D.S.C. curve with two exothermic peaks at 123 and 146°. The former peak corresponds to the formation of the 1:1 charge transfer complex (III):(V),[3] and the latter to the conversion of that complex to azobenzene (V). Accordingly, (III) gives (V) (90%) by heating at 170°.

Azobenzene (V) is reduced to phenylenediamine (I) with $SnCl_2$/aq. HCl (90%), or with Zn/NaOH in refluxing methanol (74%). (V) is converted into perchloroazobenzene[2] (VI) (Cu_2Cl_2; 63%), and into 4H,4'H-octachloroazobenzene (VII) (methanol; 96%), red crystals m.p. 259-61° through the corresponding bisdiazonium salt. (VII) analyzes correctly for C, H, N, and Cl.

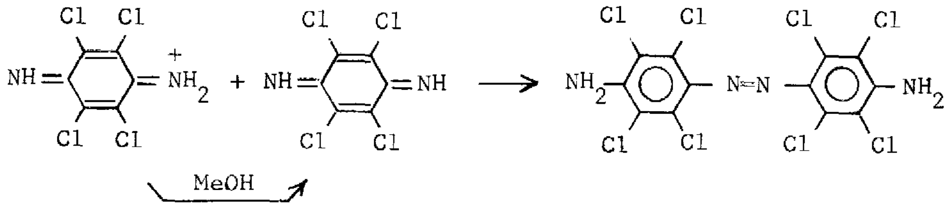
The formation of salts (II) is interpreted as follows:



$$X^- + XI \longrightarrow X_2I^- \qquad X = Cl, Br$$

According to MNDO calculations, species $Cl_2^{\dot{-}}$ corresponds to a minimum on the potential energy curve.[7]

As far as the mechanism for the remarkable formation of azobenzene (V) is concerned, it is assumed that the methanol would extract a proton from cation (II) giving diimine (III), which would immediately condense with unreacted (II). If a strong base is used, (II) reacts with it rather than with diimine (III), and consequently only (III) results, as found.



(II) (III) (V)

In this connection it is pointed out that salts (II) with NH_3 in CCl_4 give a mixture of diimine (III) and azobenzene (V). It has been ascertained that diimine (III) is inert towards methanol.

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