Isomerization of 5,6-Dihalogenocyclohex-2-ene-1,4-diones to 2,3-Dihalogeno-1,4-hydroquinones

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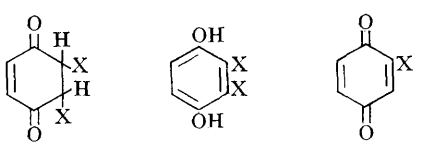
5,6-DIHALOGENOCYCLOHEX-2-ENE-1,4-DIONES (I; X = Br, Cl), usually referred to as *p*-benzoquinone dihalides, were thoroughly investigated more than 70 years ago[1] but we were unable to find any comment in the literature about the curious fact that such diketo-isomers of aromatic compounds (II; X = Br, Cl) are at all capable of existence. Further, although isomerization of (I) (or derivatives) to (II) (or derivatives) may have been involved in certain reactions[2] no systematic attempt to isomerize (I) has been described, most reagents causing facile[1] elimination to (III).

In connection with another project[3] we had occasion to prepare (I; X = Br, Cl) and a number of their derivatives, and we have confirmed their structures by n.m.r. spectroscopy.[3] We have also found that treatment of (I; X = Br) with 1 part concentrated sulphuric acid in 9 parts of acetic acid at 100° for periods of 5, 15, and 26 hours gave 41, 81, and 93% yields of (II; X = Br)[4] respectively. Similarly (I; X = Cl) gave high yields of (II; X = Cl). In the case of some derivatives of (I), the principal products were not derivatives of (II), but the coresponding 1,4-benzoquinones, presumably due to oxidation with sulphuric acid. A variety of reagents is being investigated at present.



(I) (II) (III)

It thus appears that the stability of the diketo-forms (I) with respect to their aromatic "tautomers" (II) is purely a kinetic phenomenon, the removal of an α-proton leading to elimination with formation of (III) rather than aromatization with formation of (II) unless the carbonyl group in (I) is already protonated as is presumably the case under our conditions. Once formed, (II) is completely stable with respect to (I), as expected.

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[1] T. H. Clark, *Amer. Chem. J.*, 1892, **14**, 553.
[2] (a) di A. Peratoner and A. Genco, *Gazzetta*, 1894, **24**, II, 394; (b) L. I. Smith and F. L. Austin, *J. Amer. Chem. Soc.*, 1942, **64**, 528.
[3] R. K. Norris and S. Sternhell, *Austral. J. Chem.*, in the press.
[4] New compound, whose composition and spectroscopic properties agree with the structure given.