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TRICHLOROHYDROXYQUINONE

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NUCLEOPHILIC substitution on vinyl carbon has received study recently by Vernon[1], Wallenfels[2], and others. Considerable amounts of information in this area are available in the field of quinone chemistry where the ready replacement and interchangeability of anion forming groups on the quinone nucleus is well-known. It has been suggested that the mechanism of replacement of chloride by hydroxide from the quinone nucleus proceeds by a two-step process as shown in equation (1). We wish to report that the intermediate, II, formed by the addition of hydroxide to the chloroquinone, can be readily observed and is relatively stable at high pH.

Chloranil (I) is completely insoluble in hot or cold water. Upon treatment with hot caustic it is converted readily, and in good yields, to the sodium salt of chloranilic acid (V). We have observed that solid chloranil (m.p. 294-295°, sealed tube) will dissolve quickly in ice-cold 2 M sodium hydroxide to give a pale yellow solution [λm(mμ), log ε: 250 (shoulder), 3.89; 340 (shoulder) 3.54; 365, 3.67]. Upon careful acidification, keeping cold, virtually quantitative recovery of trichlorohydroxyquinone (III) is obtained. M.p. 198-199° (uncorr.) from benzene-heptane. (Found: C, 31.66; H, 0.56; Cl, 46.00. Calc. for $C_6HCl_3O_3$: C, 31.68; H, 0.44; Cl, 46.73). Ultraviolet and visible spectrum in 1 N HCl: 295, 4.18;

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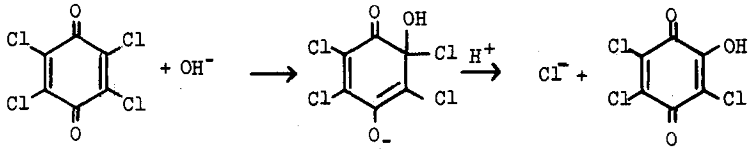
[1] D.E. Jones, R.D. Morris, C.A. Vernon and R.F.M. White, J. Chem. Soc. 2349 (1960).

[2] K. Wallenfels and K. Friedrich, Chem. Ber. 93, 3070 (1960).

449, 2.68; in water: 222, 4.22; 295, 4.09; 535, 3.16. This constitutes a previously unreported direct synthesis of III from I.

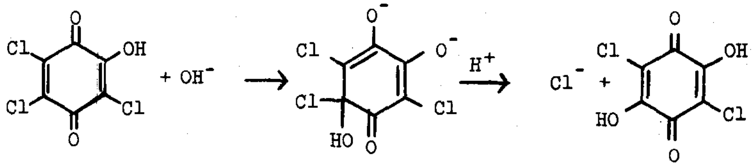
The observations confirm that the reaction proceeds as shown below, hydroxide ion adding to I to give the intermediate II which loses chloride ion slowly in the basic solution but rapidly upon addition of acid to give III.



(1)

I II III

Similar observations may be made when III, whose anion is deep purple, is dissolved in caustic solution. A yellow solution is formed which, upon acidification or heating, goes over to one from which sodium chloranilate or chloranilic acid may be isolated. The presence of an intermediate, IV, analogous to II, is consequently inferred.



(2)

III IV V

Ultraviolet and visible spectra were determined on a Cary Model 11 spectrophotometer.