

Additive Chlorination of 1-Iodonaphth-2-ol

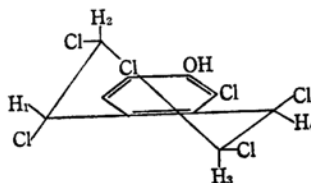
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Naphth-2-ols with a substituent at the 1-position usually react with chlorine in an additive way to yield, depending on the amount of chlorine consumed, derivatives of either 2-keto-1,2-dihydronaphthalene or 2-keto-1,2,3,4-tetrahydronaphthalene.¹⁾ An exception is 1-iodonaphth-2-ol. The conventional procedure involving chlorination in acetic acid has been found to result in the displacement of the iodine atom by chlorine, giving 2-keto-1, 1, 3, 4-tetrachloro-1, 2, 3, 4-tetrahydronaphthalene (mp 100–102°C)¹⁾ as the final product. It had strong infrared absorptions in Nujol at 722, 760, 847, 1153, and 1751 cm^{-1} . Its PMR spectrum in carbon tetrachloride at 60 Mc/sec showed two doublets, due to aliphatic protons, at 4.67 and 5.11 τ ($J=4.8$ cps) and two aromatic multiplets, at 1.70–1.95 and 2.20–2.65 τ . The formation of remarkable amounts of polymeric substances accompanied the reaction. The use of an aprotic solvent such as chloroform, however, showed another mode of chlorine addition to the naphth-2-ol system. The saturation of the solution with chlorine also led to a considerable formation of resinous by-products, and the removal of the solvent together with the iodine liberated gave a light brown syrup which, on standing, slowly separated pale yellow fine needles (mp 149–150°C after recrystallization from hot ligroin (bp 80–100°C)). Analysis showed this substance to fit the formula $\text{C}_{10}\text{H}_6\text{Cl}_6\text{O}$ (Found: C, 33.99; H, 1.72; Cl, 59.88; O, 4.72%. Calcd for $\text{C}_{10}\text{H}_6\text{Cl}_6\text{O}$: C, 33.84; H, 1.70; Cl, 59.94; O, 4.53%), and its infrared spectrum in Nujol had prominent peaks due to the $-\text{C}-\text{OH}$ group at 1192, 1416 and 3460 cm^{-1} , but no carbonyl absorption. Its PMR spectrum run in deuteriochloroform at 60 Mc/sec revealed the presence of four aliphatic protons (two doublets at 4.60 τ (H^1) and 4.38 τ (H^4), two quartets at 5.57 τ (H^2) and 4.84 τ (H^3); $J_{1,2}=3.1$ cps, $J_{2,3}=10.1$ cps, and $J_{3,4}=4.4$ cps), one aromatic proton (singlet at 2.43 τ), and a hydroxylic proton (somewhat broad) at 3.6 τ . Therefore, this adduct is a tetrachloride of a dichloronaphth-2-ol, in which two chlorine atoms

belong to an aromatic ring and four to an aliphatic ring. The high value of the coupling constant, $J_{2,3}$, shows that the 2,3-pair of C-H bonds are trans-diaxially disposed; the low values of $J_{1,2}$ and $J_{3,4}$ shows, then, that the 1- and 2-hydrogen atoms are *cis*, and that the 3- and 4-hydrogen atoms are *cis* to each other. The sharp appearance of the OH stretching absorption indicates that the hydroxyl group is blocked on both sides by chlorine atoms and is prevented from polymeric association. Thus, the α -hydrogen atom with signals in the low field is probably at the 4-position, near the chlorine atom. By analogy with the well-established α -naphthalene tetrachloride,²⁾ the stereochemistry may be formulated as below;



Considering the great tendency of naphth-2-ols to undergo additive chlorination to form ketopolychlorides, this is an unusual result. One possible explanation for such an anomaly may be that chlorine first reacts with the iodine substituent to form an unstable naphthyl iododichloride, and that the strong electron-withdrawing effect of the dichloroiodo group directs further chlorine addition in the opposite ring. Decomposition of the tetrachloride thus formed would lead to the above addition product. A similar case has earlier been reported in the spontaneous decomposition of naphth-1-yl iododichloride to 1,1,2,3,4-pentachloro-1,2,3,4-tetrahydronaphthalene and 1-chloro-4-iodonaphthalene.³⁾

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2) P. B. D. de la Mare, M. D. Johnson, J. S. Lomas and V. Sanchez del Olmo, *ibid.* (B), **1966**, 827.

3) C. Willgerodt and P. Schlösser, *Ber.*, **33**, 692 (1900).