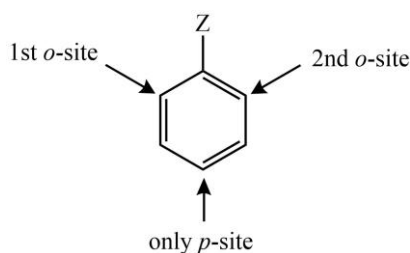


❖ The Ortho/Para Ratio

If there is an *o*-, the *p*-directing substituent on the benzene ring, the prediction of the relative amount of both products is quite difficult. This is because the attack at these sites is dictated by many factors like mathematical probability, charge density, steric effects. However, certain conclusions can still be made by considering only one factor at a time keeping others constant. In this section, we will discuss the factors affecting the ratio of *o*- and *p*-products one by one.

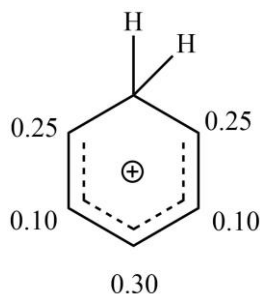
➤ Statistical Factor

One might say the relative ratio of *o*- and *p*-products should be 2:1 because there are two ortho sites but only one *p*- site. However, it is rarely obtained because the actual situation isn't that simple. For instance, consider the chlorination of methylbenzene where statistical treatment will suggest 2:1 *o*-/*p*- ratio but the actual ratio varies from 62:38 to 34:66.



➤ Charge Density

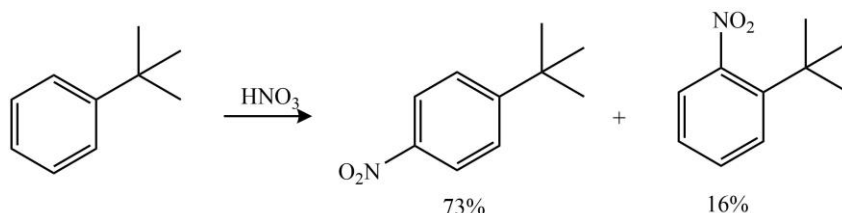
Besides statistical factors, the distribution of charge density at different carbons is of great importance in deciding the attack, which sometimes can completely outrank the former factor. For instance, the charge densities in the phenonium ion are shown below.



It is obvious from the above diagram that a para substituent would show a more significant stabilizing effect on the neighboring carbons than an ortho group. This implies that the *p*-substituted product should be more than 1/3, and the *o*-substituted product should be less than 2/3, provided that other factors like steric hindrance same in both attacks. In hydrogen exchange reactions, the ratio of partial rate factor for *o*-position to the partial rate factor for *p*-position was found to be 0.865 which quite comparable to the ratio of charge densities (i.e., $0.25/0.30 = 0.833$). Similar results were obtained (*o*-/*p*- = 67:33, though the effect was small) if the benzene had *m*-directing groups.

➤ **Steric Factors**

The attack at *p*-position is also supported by the factor steric hindrance which says that bulky will face more crowding at *o*- sites; and therefore, will try to avoid that approach. For instance, the nitration of toluene and tert-butylbenzene results in 58% *o*-product and 16% *o*-product, respectively.



➤ **Loan Pair on *o*-, *p*-Directing Group**

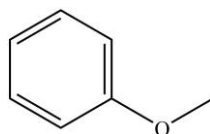
If there is a loan pair on the *o*-, *p*-directing group, the formation of *p*- product is favored at the cost of the ortho. This can be understood by considering the following example.



It is obvious that the A intermediate has an *o*-quinoid structure, whereas B intermediate has a *p*-quinoid structure; since *o*-Quinones are less stable than the *p*-Quinones, B should also be more stable than A, and hence, is expected to contribute more towards the resonance hybrid.

➤ **Substrate's Enclosing**

Although it seems impossible but exclusively *p*-products can be obtained enclosing the substrate molecules in a cavity where only the *p*- site is exposed to the electrophile. For instance, the chlorination of Anisole in solutions containing a cyclodextrin *p*/*o*- ratio of 21.656; however, only 1.48 *p*/*o*- ratio was obtained when cyclodextrin was absent.



Anisole

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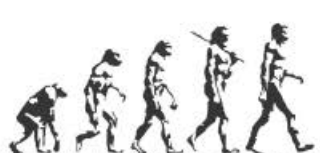
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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