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EVIDENCE FOR, AND STEREOCHEMICAL IMPLICATIONS OF INTRAMOLECULAR BASE CATALYSIS IN STERICALLY HINDERED DIAZO COUPLING REACTIONS.

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In a forthcoming publication (1) it will be shown that the σ-complex intermediates in sterically hindered diazo coupling reactions of 8-substituted 2-naphthol derivatives possess a characteristic asymmetry. The sp^3-bound hydrogen is in a pseudo-equatorial position and the electrophile pseudo-axial.

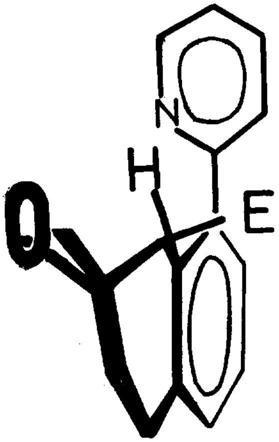
We have now found evidence for an intramolecular base catalysis in a similar reaction. The diazo coupling of 8-phenyl-2-naphthol exhibits a sterically caused (2) kinetic isotope effect (k_H/k_D = 2.7). Couplings of 8-(2'-pyridyl)-2-naphthol, however, show no such effect (3). Since the steric requirements of both substituents can be taken to be equal, the absence of the isotope effect is due to complete intramolecular base catalysis by the heterocyclic nitrogen. The size of the above effects indicates that the substituent rings are turned out of the plane of the naphthalene nucleus. A lateral approach of the basic centre to the pseudo-equatorial hydrogen atom will precede the intramolecular proton abstraction. Intermolecular base catalysis can be excluded due to steric factors (4).

It can now be said that

a) the attack of the base on the leaving proton takes place before the electrophile "swings into" the plane of the naphthalene nucleus (this process would move the proton away from the basic centre).

b) a linear σ-complex-hydrogen-base transition state is not a necessary requirement for base catalysis.

Both conclusions can readily be made on the basis of the stereochemical picture of the σ-intermediate (I).



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