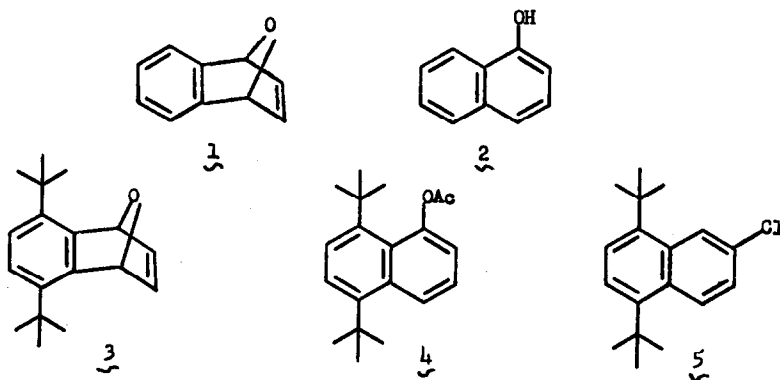


A NOVEL RESULT OF A PERI INTERACTION

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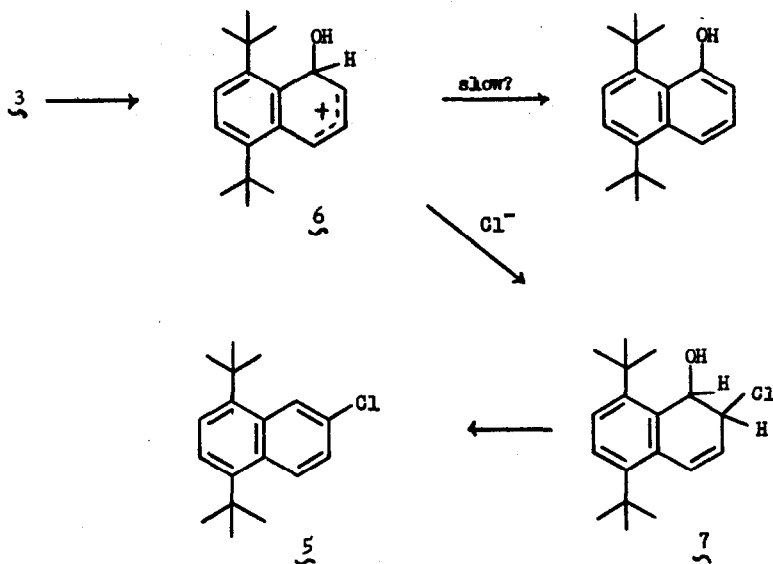
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Peri effects in 1-substituted naphthalenes are well known in a wide variety of chemical reactions.¹ We wish to describe our observations of a novel peri interaction in the rearrangement of 5,8-di-*t*-butyl-1,4-dihydronaphthalene-1,4-endoxide 3.² In the parent endoxide system 1, the rearrangement to α -naphthol 2 using methanolic HCl is a facile and quantitative conversion.³ In a parallel reaction, 3 was refluxed in ethanol saturated with HCl, and the crude, air-sensitive product was immediately acetylated with acetic anhydride. Gas chromatographic analysis revealed the presence of two major components, the naphthol acetate 4 and the chloronaphthalene 5 in 72% and 16% yield, respectively.* These products could be isolated by column chromatography on silica gel. The appearance

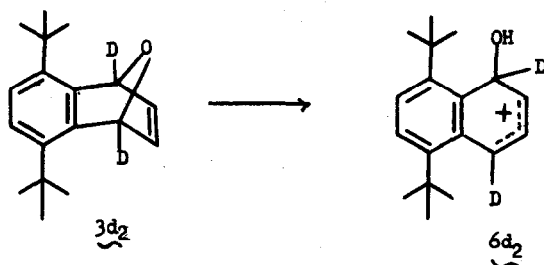


of a β substitution product in addition to the normal product can be rationalized by the following scheme (which is one of several "paper" routes). Protonation of endoxide 3 followed by ether cleavage generates the cyclohexadienyl cation 6. One could postulate that cation 6, when formed, is slow to aromatize because shortening of the C1-C9 bond and concomitant eclipsing of the hydroxyl and *t*-butyl groups raises the activation energy of the elimination

* Analyses and spectra were consistent for these structures.



step. Thus: addition of external nucleophile can become competitive,⁴ generating dihydro-naphthalene 7. (Nucleophilic attack at C₄ seems unlikely). Elimination of water from 7 would afford the observed chloronaphthalene 5. If the activation energy of the proton elimination (aromatization) from 6 is a factor in chloronaphthalene formation, then rearrangement of 3d₂ via 6d₂ should result in an observable change in product ratio. Upon rearrangement⁵ of the desired substrate 3d₂ (prepared via diazotization of 2,5-di-*t*-butylaniline in the



presence of 2,5-dideuteriofuran²) there was obtained naphthol acetate 4 in 44% yield and chloronaphthalene 5 in 39% yield. Thus, relative formation rates from a common intermediate 6 can be expressed as $(k_4/k_5)_H = 4.50$, $(k_4/k_5)_D = 1.14$, and $(k_H/k_D) 4/5 = 3.9$. The observation of a partitioning isotope effect⁶ suggests that cation 6 is an intermediate in the rearrangement of 3 and that the *peri* *t*-butyl group through a compression interaction, does indeed retard the aromatization process. This effect is analogous to the

steric effects of ortho t-butyl groups in electrophilic substitutions of benzenes.⁷

Acknowledgement We thank the National Science Foundation for support of this research.

References

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