

IPSO-ATTACK IN FREE RADICAL AROMATIC SUBSTITUTION REACTIONS

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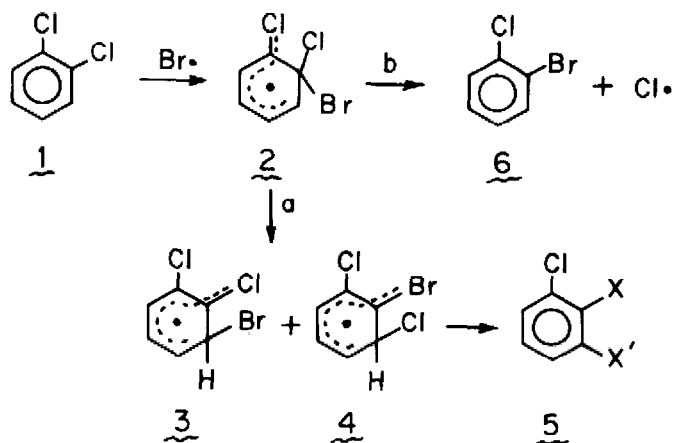
A recent report¹ of a new process, photobromination of dihalobenzenes, noted the unexpectedly large amount of ortho-substitution products and, in some cases, the extensive replacement of the original chloro substituent,² but it did not provide any explanation of these results. The purpose of this communication is to point out that these results, as well as the halogen rearrangement also implied,¹ are suggestive of ipso-attack,⁴⁻⁶ a mechanism that has not previously been advocated for free radical reactions.

During the past few years, ipso-attack has been demonstrated to be significant in some electrophilic nitrations of disubstituted benzenes.⁴⁻⁶ With acetyl nitrate or nitric acid in acetic anhydride, at least half of the nitration products obtained from p-isopropyltoluene,⁵ about 40% of those formed from o-xylene,⁶ and at least 37% of the 4-chloro-2-nitroanisole formed from 4-chloroanisole⁴ arise from ipso-attack. The ipso-intermediate leads, in varying degrees depending on original substituent, to loss of the original substituent (nitrodealkylation or nitrodechlorination) or to conventional substitution product by ortho- or meta-migration of nitro.

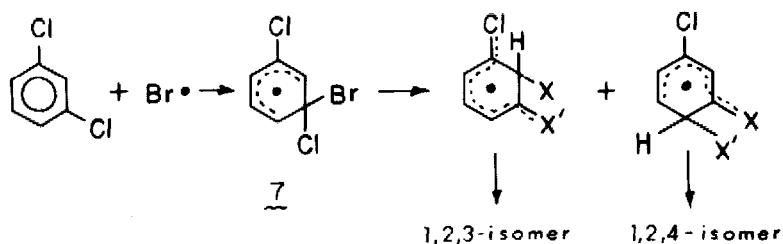
Although photobromination of chlorobenzene gave mainly m-bromochlorobenzene, only traces of meta-substitution products were obtained from 1,3-dihalobenzenes, and the usually unfavored 1,2,3-isomer was 25% of the trihalo product from that substrate.¹ With 1,2-dichlorobenzene, the 1,2,3-isomer was the main product, and bromodechlorination occurred extensively.² The report¹ implies that the

trihalobenzene products are mixtures (different halogens in different relative positions), indicating the rearrangement that is characteristic of the ipso-intermediate in electrophilic nitrations.

ipso-Attack on 1 by $\text{Br}\cdot$ would generate intermediate 2, which (a) can rearrange to intermediates 3 and/or 4, from which 1,2,3-isomer product (5) is formed; or (b) lose $\text{Cl}\cdot$ to form product 6. ortho-Migration of either geminal-



halogen⁷ in the intermediate (7) formed by ipso-attack on 1,3-dichlorobenzene can occur in two directions to give 1,2,3-isomer (25%¹) and 1,2,4-isomer (75%¹).



In addition to several halogen exchanges,^{3,9} free radical replacements of aromatic sulfonyl substituents by chlorine^{3d} and of halo by hydrogen¹⁰ have been observed. An ipso-intermediate (illustrated but not so-named) has been considered^{3d,11} for some of the chlorodebrominations but dismissed as "improbable,

requiring addition of the chlorine atom at the most unlikely spot in the aromatic system."¹¹ The data with which those earlier mechanism speculations were concerned, however, did not include mention of rearrangement products, which are particularly relevant to the ipso-mechanism.

Although halogen deactivates all positions in benzene toward electrophilic attack, the ipso-position is actually deactivated less than the other positions.⁴ Electronic effects of substituents affect rates or product distributions but little in free radical aromatic substitutions,^{8b} so there is little reason to expect ipso-attack to be disfavored for radical reactions.¹² The radical substitutions give large amounts of ortho-substitution, in comparison with most electrophilic substitutions.^{8b} ipso-Attack followed by loss or migration of one of the geminal substituents may be responsible for substantial portions of the substitution products from the radical reactions.¹³

References

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- (10) Private communication from W. A. Pryor, Feb. 11, 1976; M. G. Griffith, Ph.D. dissertation, Louisiana State University, 1968.
- (11) C. Walling, "Free Radicals in Solution", John Wiley and Sons, Inc., New York, N.Y., 1957, p. 312.
- (12) p-Bromochlorobenzene undergoes radical chlorodebromination 91% as rapidly as does bromozene; more electronegative substituents slow the reaction more.^{3d}
- (13) I gratefully acknowledge helpful suggestions about the manuscript for this Communication from my colleagues, Professors W. A. Pryor, K. N. Houk, and R. G. Gandour.