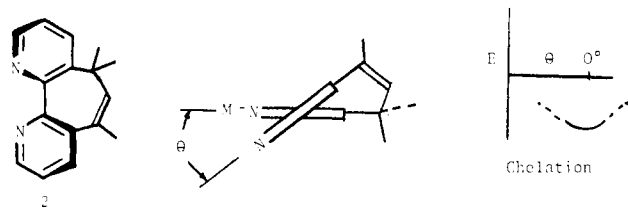


Table I. Racemization of **2**

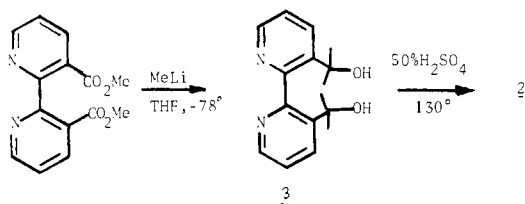
	ΔG^\ddagger	$T_c, ^\circ\text{C}$
2	14.5	2
2 ·HgCl ₂	10.5	-60
2 ·ZnCl ₂	10.5	-60
2 + 1 equiv of CF ₃ SO ₃ H	10.1	-65
2 + excess CF ₃ SO ₃ H	16.8	+68

Consider now the corresponding process in bipyridyl **2**. Again, θ defines the racemization coordinate and the transition state occurs at $\theta = 0^\circ$. The parent 2,2'-bipyridyl has been much admired for its ability to form chelates with metal ions. X-ray structures of such complexes reveal near coplanarity of the aromatic rings; i.e., maximum binding between metal and bipyridyl occurs at $\theta = 0^\circ$. Chelation and racemization share the



same coordinate, and metal ions could apply a binding force to the transition state for racemization.

We have prepared **2** from the dimethyl ester of 2,2'-binicotinic acid,⁵ readily available from the oxidation of *o*-phen-



anthroline. Excess MeLi afforded the diol **3** which cyclized to **2** under the influence of hot H₂SO₄.

The NMR spectrum of **2** showed the expected temperature effect; the dimethyl signal appeared as a broadened singlet at ambient temperature but was resolved into two singlets ($\Delta\delta = 47$ Hz) at low temperature. From the coalescence temperature ($T_c = 2^\circ\text{C}$) a barrier of 14.5 kcal/mol can be calculated. Complexes of **2** with ZnCl₂ and HgCl₂ were obtained in crystalline form and their racemization rates were determined. The kinetic parameters obtained from ¹H or ¹³C NMR spectra are presented in Table I.

As expected, the rate of racemization is enhanced in the metal complexes. The degree of enhancement reflects the difference in energy of binding in the ground-state vs. the transition-state complex. The behavior of **2** in the presence of protic acids is of special interest since true *catalysis* of racemization occurs. Observed rates increase as acid is added with the maximum rate occurring at 1 equiv. As more acid is added, rates decrease and at ~ 8 equiv the racemization rate is nearly that observed in neat CF₃SO₃H.⁶ Evidently, the dipole-dipole repulsive forces which contribute to the racemization barrier of **2** are replaced by stabilizing forces in the monoprotated form. On diprotonation, the coplanar arrangement is destabilized and racemization is inhibited.

The present examples demonstrate how remote binding forces may stabilize a transition state. Applications to chemical processes are underway.

Acknowledgment. We thank the National Institutes of Health and the A. P. Sloan Foundation for funding of this research.

References and Notes

- (1) W. P. Jencks, *Adv. Enzymol.* **43**, 219 (1975).
- (2) L. Pauling, *Chem. Eng. News*, **24**, 1375 (1946).
- (3) F. H. Westheimer in "Steric Effects in Organic Chemistry", M. Newman, Ed., Wiley, New York, N.Y., 1956, p 524; K. Mislow, S. Hyden, and H. Schaefer, *J. Am. Chem. Soc.*, **84**, 1449 (1962).
- (4) I. O. Sutherland and M. V. J. Ramsay, *Tetrahedron*, **21**, 3401 (1965).
- (5) D. Aziz and J. G. Breckenridge, *Can. J. Res., Sect. B*, **28**, 26 (1950).
- (6) Observed changes in spectra over the temperature and acidity ranges studied were completely reversible. The odd methyl resonance remains a sharp doublet throughout and shifts in the aromatic resonances are those expected for protonation exclusively on the nitrogen atoms of **2**. While the dissociation constants for protonated forms of **2** have not been determined, they should not differ greatly from *o*-phenanthroline ($pK_a = 4.5, -1.4$) or 2,2'-bipyridyl ($pK_a = 4.5, -0.5$): D. D. Perrin "Dissociation Constants of Organic Bases in Aqueous Solution", Butterworths, London, 1965, pp 331, 173.

J. Rebek, Jr.,* J. E. Trend

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received February 27, 1978

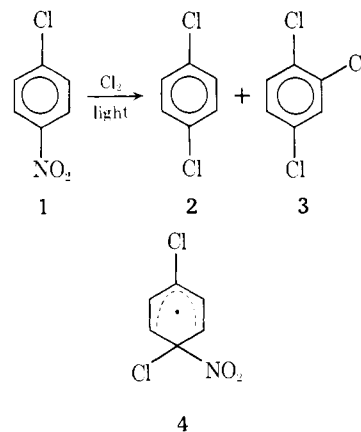
Formation and Rearrangement of Ipso Intermediates in Aromatic Free-Radical Chlorination Reactions¹

Sir:

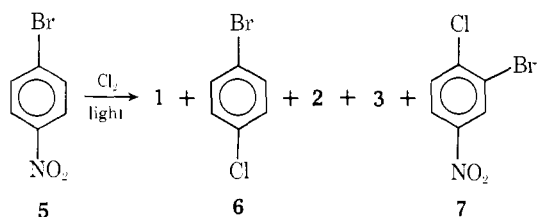
Only during the past decade has the importance of ipso attack in aromatic substitution reactions been appreciated.² Although replacements of a substituent during aromatic free radical substitution reactions have been reported by several investigators during the past 75 years,^{3,4} the substantial volume of current literature about ipso attack has been largely confined to electrophilic substitutions.² Cationic ipso intermediates have been trapped, and their rearrangements have been shown to account for as much as half of the ortho-substitution products obtained in some nitrations.² In this communication, we report evidence for the formation and rearrangement of an ipso intermediate during free-radical chlorination of *p*-bromonitrobenzene.

Ipso attack in some free-radical aromatic substitution reactions has recently been advocated,⁵⁻⁷ but firm evidence for any behavior of the proposed ipso intermediate other than loss of one of the geminal substituents (which might occur by a mechanism other than formation of an ipso intermediate) was lacking. Rearrangement of the original bromo substituent in the present case appears to require the ipso-intermediate mechanism.

Photoinitiated chlorination of *p*-chloronitrobenzene (**1**) in

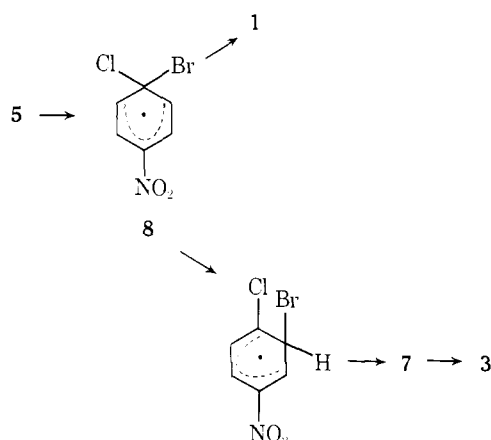


carbon tetrachloride at room temperature produces mainly *p*-dichlorobenzene (**2**) plus a small amount (2% of the amount of **2** at 57% reaction) of 1,2,4-trichlorobenzene (**3**).⁸ The reaction is mainly one of chlorodenitration, perhaps through an ipso intermediate (**4**). Photoinitiated chlorination of *p*-bromonitrobenzene (**5**) under the same conditions and at about



the same rate also produces **2** as the major product (49% at 58% reaction) plus some **3** (8% of **2** at 58% reaction), **1**, **6**, and **7**, and traces of other unidentified products.^{4,8} Chlorodebromination and chlorodenitration are competitive. During the reaction, the concentration of **1** continually increased (followed through 76% consumption of **5**), but that of **6** passed through a maximum at about 13% reaction.⁴ The production of the rearrangement product, **7**,⁸ and the greater proportion of **3** from the reaction of **5** than of **1** are particularly significant to the question of ipso intermediates.

The rearrangement product, **7**, appears to require an ipso intermediate, **8**. The product proportions reveal that loss of



bromine atom (to form **1**) is the principal fate of **8**, but some bromine migration to the ortho position does occur. The substantially increased ratios of **3:2** from **5** than from **1** strongly imply that much of **7** reacts further by ipso attacks to produce **3** more readily than **3** is produced from **2**. The actual amount of rearrangement of ipso intermediate **8**, therefore, probably exceeds by severalfold the amount of **7** detected in the reaction mixtures.¹⁰

We believe that these data establish the formation and rearrangement of an ipso intermediate in these aromatic free-radical chlorinations.

References and Notes

- Presented in part at the 33rd Southwest Regional Meeting of the American Chemical Society, Little Rock, Ark., Dec. 1977, Abstract No. 175.
- For a review, with references, see R. B. Moodie and K. Schofield, *Acc. Chem. Res.*, **9**, 287 (1976).
- (a) A. Elbner, *Ber.*, **36**, 1229 (1903); (b) G. L. Goerner and R. C. Nametz, *J. Am. Chem. Soc.*, **73**, 2940 (1951); (c) W. Voegtli, H. Muhr, and P. Lauger, *Helv. Chim. Acta*, **37**, 1627 (1954); (d) R. M. Noyes, *J. Am. Chem. Soc.*, **70**, 2614 (1948); (e) B. Milligan, R. L. Bradow, J. E. Rose, H. E. Hubbert, and A. Roe, *ibid.*, **84**, 158 (1962); (f) J. R. Shelton and C. W. Uzelmeier, *Recl. Trav. Chim. Pays-Bas*, **87**, 1211 (1968); (g) P. Gouverneur and J. P. Soumillon, *Tetrahedron Lett.*, 133 (1976).
- B. Miller and C. Walling, *J. Am. Chem. Soc.*, **79**, 4187 (1957). These authors reported that *p*-bromochlorobenzene undergoes free-radical chlorodebromination 91% as rapidly as does bromobenzene but that *p*-bromonitrobenzene does not react under the same conditions.
- J. G. Traynham, *Tetrahedron Lett.*, 2213 (1976).
- J. G. Traynham, 28th Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Oct 1976, Abstract No. 376.
- R. D. Gandour and J. G. Traynham, 173rd National Meeting of the American Chemical Society, New Orleans, La., March 1977, Abstract No. ORGN-137.
- At room temperature, ~80% of the halobenzene had been consumed after 161 h; at reflux temperature ~98% had been consumed after 34.5 h. For the room temperature process, the mass balance was 90–99% up to 57% reaction (121 h). The reactions are photoinitiated; gas chromatographic (GC) analysis of solutions of chlorine and **1** or **5** in carbon tetrachloride kept

in the dark at room temperature for 121 h showed no evidence of reaction products.

- Product **7** and its isomer, 1-bromo-2-chloro-4-nitrobenzene, were not distinguishable on three different GC columns at several different temperatures. The phenols derived from them by hydrolysis (replacement of halogen para to nitro) did have different retention times, and hydrolysis of the product mixture from **5** produced 2-bromo-4-nitrophenol but no 2-chloro-4-nitrophenol.
- GC analyses of product mixtures from **5** excluded the presence of 1,2-dichloro-4-nitrobenzene, 2,4-dichloro-1-nitrobenzene, and 1,4-dichloro-2-nitrobenzene, compounds which would have indicated chloro or nitro migration in ipso intermediates.

Charles R. Everly

Department of Chemistry, Phillips University
Enid, Oklahoma 73701

James G. Traynham*

Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

Received March 27, 1978

Heterogeneous Photocatalytic Preparation of Supported Catalysts. Photodeposition of Platinum on TiO₂ Powder and Other Substrates

Sir:

We recently described the use of platinized TiO₂ powders in the heterogeneous photocatalytic decomposition of acetic (or other carboxylic) acids to methane (or the corresponding alkanes).¹ These powders were prepared by a heterogeneous photocatalytic deposition of metal to produce a supported metal catalyst. This unique and simple method of preparation produces materials consisting of finely dispersed metal on a semiconductor support which have also been found to be useful catalysts for other processes. We describe here the preparation of catalysts of this type and discuss possible extensions and applications. There have been previous reports of photoinduced metal deposition on semiconductors.^{2–5} For example, the photovoltaic plating of silver or copper on the n side of a Si p–n junction has been described.² Photoreduction of Ag⁺ and Pd²⁺ on n-TiO₂^{3,4} and Cu²⁺ on n-TiO₂ and n-SrTiO₃ electrodes⁵ has also been investigated, frequently in connection with photographic studies. To our knowledge no previous description of these processes at dispersed powders or the application of materials prepared in this manner as catalysts has been reported.

In a typical experiment for photodeposition of metallic platinum on TiO₂ powder, 2.02 g of lightly doped anatase powder produced from undoped anatase (MCB, >99% pure by x ray; particle size 125–250 μm by sieves; grain size ~0.2 μm by scanning electron microscopy (SEM)^{1b}) was suspended in a mixture of 10 mL of platinizing solution (0.1 M hexachloroplatinic acid in 0.1 M hydrochloric acid), which had been neutralized with sodium carbonate and then brought to a pH of ~4 by addition of acetic acid. This suspension was thoroughly flushed with nitrogen to remove oxygen and CO₂ and heated to 55 ± 3 °C. The reaction mixture was irradiated with a 2500-W Hg–Xe lamp, operated at 1600 W, while a slow stream of N₂ carried the evolving CO₂ into a saturated solution of Ba(OH)₂ in 1 M NaOH, to form a precipitate of BaCO₃. After 3.6-h irradiation at 55 °C a considerable amount of BaCO₃ was trapped (after workup, 257 mg or 1.32 mmol, corresponding to an average rate of CO₂ evolution of ~400 μmol/h); the color of the originally bright orange solution had largely faded and the grayish powder had darkened significantly. A black spot of Pt was also noticed at the inside of the cell wall where the light beam was incident. Transfer of the reaction mixture, removal of reaction solution followed by repeated washing of the powder with distilled water, and finally