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Formation and Rearrangement of Ipso Intermediates in Aromatic Free-Radical Chlorination Reactions[1]

Charles R. Everly and James G. Traynham*

Contribution from the Departments of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, and Phillips University, Enid, Oklahoma 73701

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Photoinitiated chlorination of *p*-chloronitrobenzene (**1**) in carbon tetrachloride at room temperature produces mainly *p*-dichlorobenzene (**2**) plus some 1,2,4-trichlorobenzene (**3**). Reaction of *p*-bromonitrobenzene (**7**) under the same conditions also produces **2** and **3** plus a small amount of 1-chloro-2-bromo-4-nitrobenzene (**9**). The presence of rearrangement product **9** and the greater ratio of **3**/**2** from **7** than from **1** are strong evidence for the formation and rearrangement of an ipso intermediate (**10**) in these aromatic free-radical chlorinations.

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, 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] We have now obtained evidence for the formation and rearrangement of an ipso intermediate during free-radical chlorination of *p*-bromonitrobenzene.

Although the ipso position has been regarded by some investigators as the most unlikely position for attack by a free radical and although a significant role for an ipso intermediate in the mechanism of aromatic free-radical substitution reactions has been advocated only recently,[1b,3-5] the chemical literature includes a number of reports of free-radical ipso substitutions. The earliest one appears to be about the formation (in 50% yield) of chlorobenzene by the chlorination of bromobenzene,[6] and several reports of similar halogen exchanges in preference to or at least competitive with hydrogen replacement have followed.[7] Replacements of halo substituents in benzene derivatives by (4-bromophenyl)diphenylmethyl radical,[8] by aryl radicals,[9] by cyclohexyl radical,[10] by elemental sulfur (presumably as a diradical intermediate),[11] by benzenesulfenyl and benzenesulfonyl radicals,[12] and by hydrogen atom,[13] replacement of the chloro substituent in 9-chloroanthracene by phenyl radical,[14a] and replacements

* Address correspondence to Louisiana State University.

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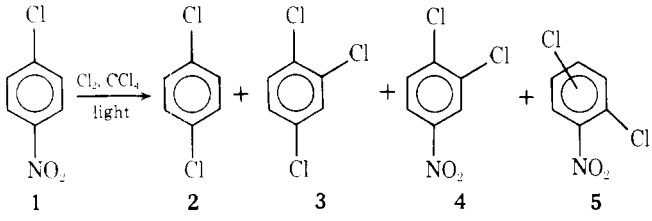
in benzene derivatives of arenesulfonyl by chlorine,[7c] of methoxy by 3,4,5-trimethoxyphenyl radical,[15] and of nitro by triplet methanesulfonylnitrene[16] have been reported. A variety of 2 substituents in 1-thia-3-azaindenes (benzothiazoles) have been replaced by adamantyl and acetyl radicals; the lowest yields were obtained with 2-halo substituents.[17] Ipso substitution of and relocation (to 2 position) of a phenyldiazenyl substituent in 4-phenyldiazenyl-1-naphthol by chlorine from *tert*-butyl hypochlorite in chloroform solution have been reported, but speculation about the reaction mechanism was meager.[18] Several phenol oxidations give products which appear to arise from ipso attack by substituted phenyl radicals,[14b] and some natural product syntheses appear to have depended on such reactions.[19] Lead tetraacetate oxidation of several 2′-substituted 2-biphenylcarboxylic acids leads to loss of the 2′ substituent as a lactone is formed; this process has been interpreted as ipso attack at the 2′ position by a carboxy radical intermediate.[20] Similar results have been obtained in mass spectral studies of 2′-nitro- and 2′-carboxy-2-biphenylcarboxylic acids,[21] but these processes have been described alternatively as ipso attack by $-C(^{+}OH)O^{\cdot}$[21a] and as prior loss of the 2′ substituent to generate a substituted phenyl cation intermediate.[21b]

In some, but not all, of the above reports, the concept of an ipso intermediate (or transition state) was considered, even though the term "ipso" was seldom used. As is indicated by the alternative proposals for the mass spectral studies,[21] mechanisms other than ipso attack by a free radical to form an ipso intermediate are conceivable in many of these cases. No firm evidence for any behavior of a (proposed) ipso intermediate other than loss of one of the geminal substituents was reported, and this behavior alone does not require such an intermediate. Rearrangement of the original bromo substituent in the present case appears to require the ipso intermediate mechanism.

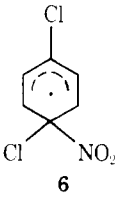
Results and Discussion

Photoinitiated chlorination of *p*-chloronitrobenzene (**1**) in carbon tetrachloride at room temperature produces as the main product *p*-dichlorobenzene (**2**) plus a small amount of 1,2,4-trichlorobenzene (**3**) and, after long reaction times, detectable amounts of 1,2-dichloro-4-nitrobenzene (**4**) and another product which was probably 2,4-dichloro-1-nitrobenzene and/or 1,4-dichloro-2-nitrobenzene (**5**).[22] A summary of the



product distributions through the progress of the reaction is presented in Table I.

The reaction is mainly one of chlorodenitration, perhaps through an ipso intermediate (**6**). The small amount of **3** obtained could be formed from **2** or **4**. Since **2** is the main product, indicating that nitro replacement is much more favored than hydrogen replacement, and only traces of **4** can be detected after long reaction times, we believe that virtually all of **3** is produced by further chlorination of **2**.



6

Table I. Chlorination of 1 in CCl_4 at Room Temperature

time, h	1[a]	2[a]	3[a]
16.75	0.899	0.071	
28.75	0.888	0.099	
40.75	0.837	0.134	
55.25	0.758	0.260	0.002
83.00	0.533	0.385	0.006
121.00[b]	0.428	0.482	0.011
161.00[b]	0.178	0.640	0.026

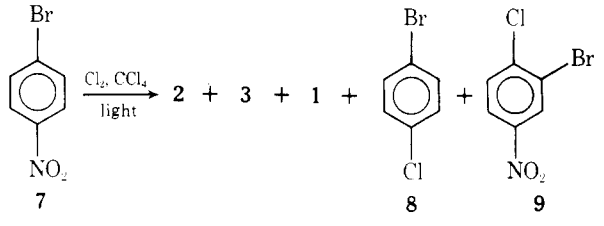
[a] Mole equivalents based on initial concentration of **1** (0.1248 M). [b] Two additional GC peaks, corresponding to trace amounts of **4** and **5**, were detected at these times.

Table II. Chlorination of 7 in CCl_4 at Room Temperature

time, h	7[a]	2[a]	3[a]	1[a]	8[a]
16.75	0.923	0.024		0.020	0.029
28.75	0.872	0.035		0.025	0.032
40.75[b]	0.873	0.050		0.039	0.035
55.25[b]	0.696	0.114	0.003	0.077	0.027
83.00[b]	0.501	0.237	0.011	0.104	0.031
121.00[b]	0.419	0.287	0.023	0.141	0.027
161.00[b]	0.235	0.434	0.049	0.160	0.016

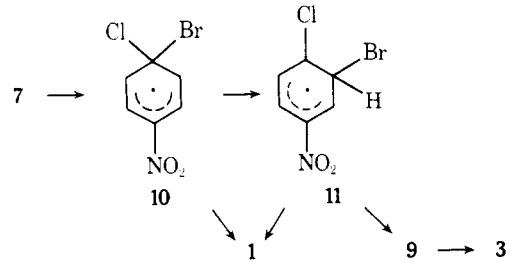
[a] Mole equivalents based on initial concentration of **7** (0.1002 M). [b] Traces of **9** were detected by GC analysis at these times; less than 10^{-3} mol equiv.

Photoinitiated chlorination of *p*-bromonitrobenzene (**7**)



under the same conditions and at about the same rate also produces **2** as the main product.[23] The product distributions through the progress of the reaction are summarized in Table II. Chlorodebromination (to give **1**) and chlorodenitration (to give **8**) are competitive. During the reaction the amount of **1** continually increased (followed through 76% consumption of **7**), but that of **8** passed through a maximum at about 13% reaction.[24] The amount of **3**, relative to the amount of **2**, from the chlorination of **7** is 3–4 times that from the chlorination of **1**. This greater proportion of **3**, which implies a more favorable route to **3** from **7** than from **1**, and the detection of rearrangement product **9** are particularly significant to the question of ipso intermediates.

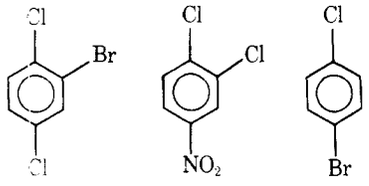
The rearrangement product, **9**, appears to require an ipso intermediate, **10**. The product proportions reveal that loss of



bromine atom (to form **1**) is the principal fate of **10**, but some bromine migration to the ortho position does occur (intermediate **11**). The substantially larger ratios of **3**/**2** from **7** than

from 1 strongly imply that much of 9 reacts further by ipso attacks to produce 3 more readily than 3 is produced from 2. (Fast replacement of bromo ortho to bromo has been reported previously.[10b]) If any of intermediate 11 goes to stable product by loss of bromine rather than by hydrogen atom (to form 1), the extent to which the formation of 11 is perceived will be reduced by that amount. The actual amount of rearrangement of ipso intermediate 10, therefore, probably exceeds substantially the amount of 9 detected in the reaction mixtures (up to 35-fold on the basis of increased proportion of 3 alone).[25]

Pairs of substituted halobenzenes were chlorinated competitively by the same procedure used for 1 and 7 individually. These experiments showed that 2-bromo-1,4-dichlorobenzene (12) reacts over 100 times as rapidly as does 2, that 1,2-di-



12 13 14

chloro-4-nitrobenzene (13) reacts about 6 times as rapidly as does 2, and that 1-bromo-4-chlorobenzene (14) reacts about 20 times as rapidly as does 1. These data demonstrate that, in these polysubstituted benzenes, the bromo substituent is much more readily replaced by chlorine than nitro and hydrogen are and that the conversion of 9 to 3 is as likely as was inferred above.

We believe that these data establish the formation and rearrangement of an ipso intermediate in these aromatic free-radical chlorinations and strongly imply that similar intermediates play significant roles in other aromatic free-radical substitution reactions.

Experimental Section

NMR data were obtained with a Varian Associates A60A spectrometer, and chemical shifts are reported relative to internal tetramethylsilane. Gas chromatographic (GC) data were obtained with a Hewlett-Packard 700 instrument equipped with a hydrogen flame detector or with a Sargent-Welch instrument equipped with a thermal conductivity detector; aluminum columns packed with Carbowax 20M on Chromosorb P (1.8 m), with SE-30 on Chromosorb P-AW (3 m), or with Apiezon L on Chromosorb P-AW (2.7 m) were used for all GC analyses. Element microanalyses were performed by R. Seab, Louisiana State University. Carbon tetrachloride was distilled and stored over 4Å molecular sieves. All GC reference compounds, except those whose syntheses are described below, were used as purchased.

Chlorinations. In a round-bottom flask equipped with a reflux condenser, a drying tube, and a magnetic stirrer a stirred mixture of a solution of 1 (6.24 mmol) or 7 (5.01 mmol) in carbon tetrachloride (50-mL total volume) and 0.5 mL (~22 mmol) of liquid chlorine was irradiated at room temperature by a 150-W tungsten lamp placed 4 in. from the flask. Portions of the solution were removed at various times, quenched with 5% sodium thiosulfate solution, washed with saturated sodium bicarbonate solution and water, dried (4Å molecular sieves), and analyzed by GC. In reactions with 7, the mixture developed a faint bromine color after some time; the entire (remaining) mixture was then quenched, washed, dried, and recharged with chlorine, and irradiation and reaction were resumed. At least three analyses per sample portion were averaged to give the data summarized in Tables I (1) and II (7).

Similar chlorinations were carried out at reflux temperature; the heating was supplied by the 150-W tungsten lamp placed 0.5 in. from the flask. The reactions proceeded more rapidly and the mass balances were lower (probably because of unmeasured polychlorination products), but otherwise the reactions gave results comparable with those obtained at room temperature.

Pairs of compounds (12 and 2, 13 and 2, 14 and 1; 1 mmol of each in 25 mL of CCl_4) were chlorinated competitively at about 30 °C by the same procedure; the relative rates of reaction were estimated from the loss of reactants as revealed by GC analysis. Compound 12 was completely consumed before reaction of 2 was detected (replacement of Br vs. H), 13 reacted 6.4 ± 0.8 times as fast as 2 (NO_2 vs. H), and 14 reacted 20.5 ± 2.4 times as fast as 1 (Br vs. NO_2).

2-Bromo-1-chloro-4-nitrobenzene (9). A sample of 9 was prepared by heating a mixture of 1, iron powder, and bromine (added slowly) at about 100 °C for 2 h and was recrystallized from EtOH: mp 57.5–58 °C; ^1H NMR (CCl_4) δ 7.5–8.5 (ABC m). Anal. Calcd for $C_6H_3BrClNO_2$: C, 30.48; H, 1.28; N, 5.92. Found: C, 30.21; H, 1.13; N, 5.66.

1-Bromo-2-chloro-4-nitrobenzene. 2-Bromo-5-nitroaniline (mp 139–140.5 °C) was prepared from *m*-nitroaniline, dilute hydrochloric acid, and hydrogen peroxide[26] and was converted to the diazonium chloride in aqueous solution. One-half of the cold diazonium chloride solution was treated with a solution of copper(I) chloride in concentrated hydrochloric acid to form 1-bromo-2-chloro-4-nitrobenzene: mp 61.5–62.5 °C; ^1H NMR (CCl_4) δ 7.7–8.4 (ABC m). Anal. Found for $C_6H_3BrClNO_2$: C, 30.16; H, 1.19; N, 5.70.

The other half of the diazonium chloride solution was reduced with 50% hypophosphorous acid to give 7, mp 125.5–126.5 °C. This reaction confirms the desired orientation in the bromination of *m*-nitroaniline.

Hydrolyses of Bromochloronitrobenzenes. A solution of 1-bromo-2-chloro-4-nitrobenzene, 50% aqueous EtOH, and NaOH was refluxed for 19 h, cooled, neutralized with 6 M HCl, and extracted with CCl_4. After the extract had been washed and dried (4Å molecular sieves), GC comparison with purchased samples showed that the hydrolysis product was (as expected) 2-chloro-4-nitrophenol, distinguishable from 2-bromo-4-nitrophenol.

In a similar fashion, the residue obtained by removing solvent from the CCl_4 solution of the product mixture from the chlorination of 7 was hydrolyzed with sodium hydroxide. GC analysis of the extract showed the presence of a small amount of 2-bromo-4-nitrophenol and no detectable amount of 2-chloro-4-nitrophenol.

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Registry No.—1, 100-00-5; 2, 106-46-7; 3, 120-82-1; 4, 99-54-7; 5, 69532-88-3; 7, 586-78-7; 8, 106-39-8; 9, 16588-26-4; 12, 1435-50-3; 1-bromo-2-chloro-4-nitrobenzene, 29682-39-1; 2-bromo-5-nitroaniline, 10403-47-1; *m*-nitroaniline, 99-09-2; 2-chloro-4-nitrophenol, 619-08-9; 2-bromo-4-nitrophenol, 5847-59-6.

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(23) The reactions are photoinitiated; GC analysis of solutions of chlorine and **1** or **7** in CCl_4 kept in the dark at room temperature for 121 h showed no evidence of reaction products.
(24) *p*-Bromochlorobenzene was reported to undergo free-radical chlorodebromination 91% as rapidly as did bromobenzene, and *p*-bromonitrobenzene was reported not to react under the same conditions.[7c]
(25) GC analyses of product mixtures from **7** 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.
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Acid-Catalyzed Dimerization of 10-Methyleneanthrone. Synthesis of Spiro-Substituted Benz[*de*]anthracenes

Hans-Dieter Becker* and Domingo Sanchez

Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg, Sweden

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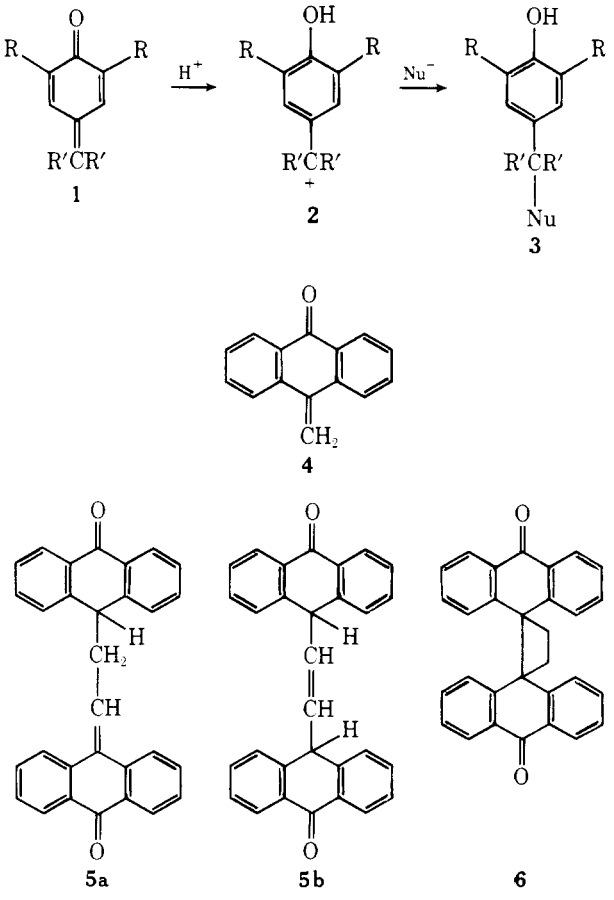
The acid-catalyzed dimerization of 10-methyleneanthrone is found to give 7′-hydroxy-1′,2′-dihydrospiro[anthracene-9(10H),3′-[3*H*]benz[de]anthracen]-10-one (**9a**), which in solution is in equilibrium with its keto tautomer **9b.** Previously proposed structures of the methyleneanthrone dimer are thus being corrected.

p-Quinone methides **1,** in general, are prone to undergo acid-catalyzed reactions with nucleophiles (Nu) to give 1,6-addition products **3** via intermediate hydroxybenzyl cations **2.**[1–3] By contrast, treatment of 10-methyleneanthrone (**4**) with acids at elevated temperature was reported to give a dimer believed to have structure **5a** or **5b.**[4] According to a very recent reinvestigation, this dimer is suggested to have the spiro-substituted cyclobutane structure **6.**[5] However, no evidence whatsoever in support of this structure has been presented.

We had reasons to doubt the correctness of the dianthronylethylene structure **5b** when we recently succeeded in synthesizing the tautomer **7** and found it to be easily dehydrogenated by molecular oxygen to give dianthronylideneethane (**8**) rather than tautomerizing to **5b.**[6]

Repeating the acid-catalyzed reaction of 10-methyleneanthrone according to the literature[4] did afford, though rather sluggishly, the reported dimeric product; however, its 270-MHz NMR spectrum turned out to be incompatible with any of the previously proposed three structures. Therefore, we have reinvestigated the acid-catalyzed reaction of 10-methyleneanthrone and found that the dimerization proceeds smoothly at room temperature in chloroform in the presence of trifluoroacetic acid or boron trifluoride etherate. In the present paper we describe the structure of the 10-methyleneanthrone dimer prepared by this method and its utilization in the preparation of spiro-substituted benz[*de*]anthracenes.



Results and Discussion

10-Methyleneanthrone dimerizes upon treatment with trifluoroacetic acid or boron trifluoride etherate in chloroform solution under nitrogen to give, in about 80% yield, the spiroanthronyl-substituted dihydrobenzanthracene **9a,** which, in solution, is in equilibrium with its keto tautomer **9b.** In the crystalline state, the 10-methyleneanthrone dimer predominantly exists in the keto form, as we conclude from the absence of a hydroxyl absorption in its IR spectrum.

It is essential to carry out the dimerization of 10-methyleneanthrone in an inert atmosphere. In the presence of oxy-

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