Isomeric Distributions and Relative Reactivities in the Uncatalyzed Chlorination of Benzonitrile, Nitrobenzene, and Benzotrifluoride. The Directive Effects of Electron-Withdrawing Substituents as a Function of Reagent and Solvent

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Abstract: The isomeric distributions and relative reactivities for the uncatalyzed chlorination of benzotrifluoride, benzonitrile, and nitrobenzene in acetic acid have been determined by a combination of vpc and radiochemical techniques. The reactivity order is: $C_6H_5CF_3 > C_6H_5CN > C_6H_5NO_2$, and a linear free-energy correlation is observed with $\rho = -6.6$. The 1 : 2 meta : para ratios decrease in the order $CF_3 > NO_2 > CN$, which is not the order of the deactivating power of the substituents, whereas, as it is expected, ortho reactivity significantly exceeds para reactivity for CN and NO_2 groups. For CF_3 groups the 1 : 2 ortho : para ratio is near unity. Comparison of the isomeric distributions obtained in the present work with those determined for the reactions of the same substrates with "Cl$^+$" and NO_2^+ reveals that the nature of the reagent has little effect on the isomeric distribution of benzotrifluoride, whereas for nitrobenzene and benzonitrile the "positive" reagents exhibit a *larger* selectivity and a stronger meta orienting power than molecular chlorine. It is suggested that under the reaction conditions when "Cl$^+$" and NO_2^+ are used as electrophilic reagents, the electronic properties of the CN and NO_2 groups (which are very strong electron acceptors) are substantially modified by interaction with the protic solvent and/or the reagent. A possible intervention of a "charge effect" is also considered. Therefore, orientation data obtained with these charged reagents would not reflect the effects of the essentially unperturbed CN and NO_2 groups in electrophilic aromatic substitutions.

Electrophilic aromatic substitution has been the subject of many investigations, both physical–organic[4–6] and theoretical[7] in nature. Although current theories of substituent effects are generally satisfactory,[8] there are still some areas of investigation which remain unexplored and for which the existing theories have to be tested.

One of these areas concerns the reactions of mild, uncharged reagents such as molecular halogens with benzene derivatives of the type C_6H_5X, X being an electron-attracting, unsaturated group (CN, NO_2, etc.) or, more generally, a strongly deactivating group. The present notion of the meta orienting power of groups of this type relies exclusively upon reactions such as nitration and chlorination carried out under conditions where a charged electrophile (NO_2^+ and "Cl$^+$," respectively) is thought to be involved. In both these reactions a high proportion of the meta isomer is formed and 1 : 2 meta : para ratios are on the order of ten or greater. With milder reagents the reactions are so slow that neither their rates nor isomeric ratios can be determined by traditional techniques.[9]

We were prompted to obtain such data, especially isomeric ratios, by the fact that our study of the electrophilic aromatic substitution of polymethylbenzenes[10] yielded unexpected information about the directive effect of the cyano group in uncatalyzed halogenations by molecular halogens ($X_2 = Cl_2, Br_2$).[10,11] From these data it was implied that the meta and para positions in benzonitrile could be deactivated *in these reactions* to about the same extent. This result has puzzled many investigators, and has led to diverse hypotheses, such as the possible breakdown of the additivity principle[12] and steric hindrance to solvation.[13] Also, despite the generally high precision of the PMB method,[10] it could be argued that the above deduction on the meta *vs.* para isomeric distribution for benzonitrile may suffer from the evaluation of a small difference (meta *vs.* para reactivity) from large numbers (the very strong deactivating effects of the cyano group at all ring positions).

In recent years, a noticeable progress has been made in the field of highly precise techniques for use in product analysis. In particular, two of us have developed and successfully applied[14,15] a method resulting from a

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(12) See ref 4, p 146.

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combination of vpc and radiochemical techniques. In this paper we wish to report results on the determination of isomeric ratios in the uncatalyzed chlorination of benzonitrile, nitrobenzene, and benzotrifluoride. Data on the relative reactivities are also presented.

Results

The chlorination reactions were carried out in 80% (by volume) aqueous acetic acid, being left for several months in the dark at room temperature. The reactant concentrations were about 1 *M* for the benzene derivative and 0.65 *M* for chlorine. These conditions are suitable for the uncatalyzed reactions with molecular chlorine.

The isomeric proportions were determined by an isotopic dilution method using $^{36}Cl_2$ and fractionation with a preparative vpc apparatus. By this technique it was possible to obtain data on isomeric distributions with reasonable precision, even if in some reactions the percentage of conversion was about 0.01%. Details are reported in the Experimental Section. The present results are collected in Table I.

Table I. Isomeric Distributions for the Chlorination by Molecular Chlorine of Some Deactivated Monosubstituted Benzenes in Aqueous Acetic Acid at Room Temperature[a]

Substituent	% ortho	% meta	% para
CF_3	9.0	86.3	4.3
CN	34.0	55.2	10.6
NO_2	24.1	68.7	7.1

[a] The probable errors are 8, 2, and 14% for ortho, meta, and para percentages, respectively.

Relative reactivities of the substrates, as measured by competitive experiments, are reported in Table II, and provide for the first time quantitative data concerning highly deactivated molecules with mild electrophilic reagents. In Table II the relative reactivities of the single positions are also reported (with respect to the reactivity of the position para to the nitro group), which are obtained by appropriate combination of the values of the isomeric distribution and "overall" relative reactivity.

Table II. Relative Rates for the Chlorination by Molecular Chlorine of Some Deactivated Monosubstituted Benzenes

Substituent	Overall rel rate[a]	Rel rate per single position[b]		
		Ortho	Meta	Para
CF_3	19.5	12.35	118.0	11.8
CN	4.2	10.00	16.3	6.3
NO_2	1.0	1.70	4.8	1.0

[a] Relative to nitrobenzene. [b] Relative to the position para to the nitro group.

Discussion

Reactivity Data with Molecular Cl_2. The reactivity order $C_6H_5CF_3 > C_6H_5CN > C_6H_5NO_2$, shown in Table II, is that expected on the basis of the electron-attracting power of the substituents. The relative reactivities of the meta and para positions satisfactorily fit a Hammett-type equation, σ_p^+ and σ_m^0 being used as the substituent constants[16] (Figure 1).

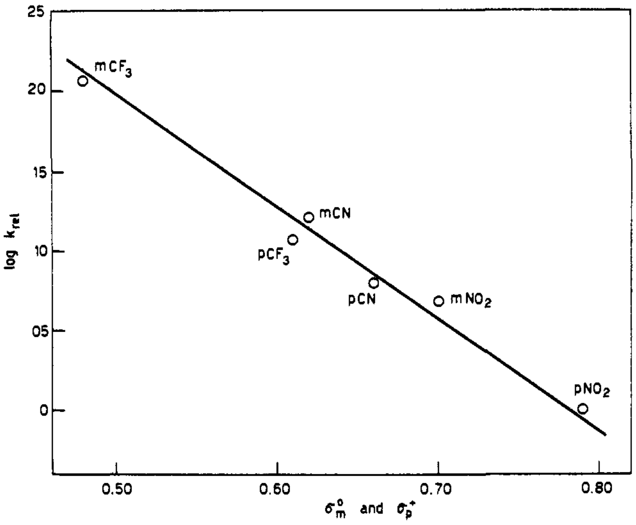

Figure 1. Hammett-type plot for reactivities at meta and para positions relative to that para to the NO_2 group (chlorination with Cl_2 of monosubstituted benzenes).

From this plot it is possible to calculate a value of $\rho = -6.6$, which is, considering the very small range of reactivities investigated and the experimental difficulties involved in the present determination, in reasonable agreement with the ρ value (-7.8) calculated by Yukawa, Tsuno, and Sawada[17] on the basis of reactivity data for the chlorination of meta substituted benzenes. Also, a reasonably linear free-energy relationship is found between the present data for the chlorination of benzotrifluoride and nitrobenzene and those for the protodegermylation of meta and para nitro and trifluoromethyl substituted triethylphenylgermanes.[18] From the slope, a ρ value of -7.3 can be calculated for the chlorination reaction.

Orientation Ratios with Molecular Cl_2. Orientation ratios (1 : 2 meta : para and 1 : 2 ortho : para) are collected in Table III, together with corresponding values for nitration and Ag^+-catalyzed chlorination. Out of the diverse data available on the isomeric distributions for the nitration of nitrobenzene, those recently obtained by Mésure and Tillet[19] using modern analytical techniques are preferred to the generally quoted data of Holleman.[20] Data for the chlorination by molecular chlorine show that the order of meta orienting power (1 : 2 meta : para ratio), $CF_3 > NO_2 > CN$, is not strictly the order of deactivating power, $NO_2 > CN > CF_3$. Even though a parallelism between the meta orienting power and the deactivating effect is invoked by current theories of orientation for -I and -R substituents,[21] it should be noted that it cannot be anticipated on the basis of the differences between σ_m and σ_p values of substituents of -I and -R types and is in contrast with other experimental evidence. Thus, in the nitration of benzonitrile, benzaldehyde and nitrobenzene,[22] the 1 :2

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(19) A. D. Mésure and J. G. Tillet, *J. Chem. Soc. B*, 669 (1966).

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(21) Reference 6, pp 40, 46–47, 306–307.

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Table III. Orientation Ratios for Chlorination and Nitration of Some Deactivated Monosubstituted Benzenes

	Chlorination by Cl_2[a]		Chlorination by Cl_2[b] (PMB approach)	Chlorination by Cl^+[c]		Nitration	
Substituent	1:2 ortho:para	1:2 meta:para	1:2 meta:para	1:2 ortho:para	1:2 meta:para	1:2 ortho:para	1:2 meta:para
CF_3	1.04	10.0		1.93	10.0	1.00[d]	15.1[d]
CN	1.6	2.6	1.7	4.0	12.7	3.7[e]	20.9[e]
NO_2	1.7	4.8		5.9	26.6	1.7[f]	33.7[f]

[a] This work. [b] Data from polymethylbenzene approach; uncatalyzed chlorination in acetic acid at 30°, ref 9. [c] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3610 (1961); Ag^+-catalyzed chlorination in CCl_4–$HClO_4$ mixture at 25°. [d] R. J. Albers and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **83**, 930 (1964); nitration in mixed acids. [e] J. P. Wibaut and R. Van Strick, *ibid.*, **77**, 316 (1958); nitration in HNO_3–H_2SO_4 mixture at 0°. [f] Reference 19; nitration by HNO_3–H_2SO_4 mixture at 0°.

meta:para ratio is in the order $NO_2 > CHO > CN$, which is not the expected order of deactivating power, and in the protodegermylation reaction of triethylphenylgermanes,[18] the differences between the meta and para reactivities are very similar for CF_3 and NO_2 groups.

The interaction of the substituent with the ring, in the ground state, is likely to play a role in determining the 1:2 meta:para ratios. In the present case, the CF_3 group may exhibit the largest –R effect, thus producing a greater discrimination between meta and para position than CN and NO_2 groups. The nature of the –R effect of the CF_3 group is still a matter of discussion; however, very recent results have given support to the hypothesis of a fluoride ion hyperconjugation.[23]

As to the 1:2 ortho:para ratios, ortho reactivity is found to exceed significantly para reactivity with the CN and NO_2 groups (1:2 ortho:para = *ca.* 1.7). This is quite an expected result, since electron-withdrawing substituents of the –I, –R type are known to give high proportions of the ortho isomer. In recent years there has been an increasing tendency to consider ortho reactivities in electrophilic aromatic substitutions as being mainly determined by electronic effects,[24] with very little allowance being made, except in special cases, for the operation of the so-called "proximity effects"; thus, the high 1:2 ortho:para ratios, observed for –I, –R substituents have been explained,[24a] on the basis of reasoning similar to that used to explain 1:2 meta:para ratios.[21] Such an explanation, however, cannot be entirely valid in our case, since no close parallelism is observed between the 1:2 ortho:para and 1:2 meta:para ratios. The possibility of an interaction between the substituent and the reagent, especially favoring substitution at the ortho position, has been assumed previously.[25] Although this hypothesis has not been proved and has been subject to criticism,[7,26] we believe that it should be reconsidered in the light of the present results.

Comparison with Charged Electrophiles. Some Remarks on the Selectivity Concept. The isomeric ratios (1:2 ortho:para and 1:2 meta:para) obtained in the present study for the chlorination by molecular chlorine of benzonitrile, nitrobenzene, and benzotrifluoride are compared (Table III) to those obtained in the nitration and Ag^+-catalyzed chlorination of the same substrates, *i.e.*, in reactions where the positive species NO_2^+ and "Cl^+,"[27] respectively, are thought to be involved. With the CF_3 group, the 1:2 meta:para ratios are the same for Cl_2 and "Cl^+," a slightly larger value being observed when the reagent is NO_2^+. With both CN and NO_2 groups, the data of Table III show that the 1:2 meta:para ratios for nitration and Ag^+-catalyzed chlorination are significantly larger than those found for uncatalyzed chlorination.

The 1:2 ortho:para ratios tend to be higher for the reactions with the charged reagents; however, no clean-cut generalization can be made with the data at hand. For this reason and because the 1:2 meta:para ratios are more simply correlated to the "selectivity" of the reagent than the 1:2 ortho:para values, we will restrict our attention in the present discussion to the former only.

A major result stemming from the present data is that on passing from a very reactive, charged, or highly polarized species to the less-polarized, milder Cl_2, the meta orienting power of a –I, –R substituent is *practically unchanged* (CF_3) or *greatly reduced* (CN and NO_2). For the CN group this finding is in substantial agreement with the one previously obtained from the PMB approach, which yielded a calculated value as low as 1.7.

The concept of reagent selectivity has been set forth by Stock and Brown,[28] essentially on the basis of the orienting effects of the methyl group, and can be easily applied to all +R substituents. In such a case the meta *vs.* para discrimination is due to the fact that the substituent can stabilize, by a conjugative electron-releasing mechanism, the transition state leading to the para substituted product better than that which leads to the meta substituted product; it will increase as the extent of bond formation in the transition state increases, which generally occurs on going from a very reactive, low electron demanding reagent, such as the positive species, to a mild, neutral reagent of high electron requirement.

We note that for –R groups no corresponding effects are expected for two main reasons. First, the resonance interaction between an –R substituent and the ring in the ground state does not increase in the transition state. Second, since –R substituents are strongly de-

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(23) G. Grinkiewicz and J. H. Ridd, *J. Chem. Soc. B*, 716 (1971).

(24) (a) Reference 6, p 305; (b) ref 4, p 82; M. Charton, *J. Org. Chem.*, 34, 278 (1969).

(25) A. P. Lapworth and R. Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, 72, 243 (1928); G. S. Hammond and M. F. Hawton in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 180.

(26) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p 314.

(27) Although little is known about the nature of the halogenating species in the Ag^+-catalyzed chlorination, the intervention of a charged or highly polarized species, $Cl^{+\delta}\cdots X^{-\delta}$, is suggested by several observations; see E. Berliner, *J. Chem. Educ.*, 43, 124 (1966). For the sake of simplicity, such species will be referred to as "Cl^+."

(28) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, 1, 35 (1963).

activating the transition states may be thought to resemble closely the intermediate σ complexes (nearly complete bond formation) even with the less selective, more reactive reagents. This is also clearly shown by the fact that in nitration the reactivity ratio *p*-nitrotoluene: nitrobenzene is much larger than the reactivity ratio toluene: benzene,[29] and approaches the toluene: benzene ratio observed in molecular chlorinations. As a consequence, with strongly deactivated substrates, changes in the extent of bond formation and therefore in the meta *vs.* para discrimination on changing reagent selectivity probably are not very important.

The data for the reactions of benzotrifluoride with Cl_2, "Cl^+," and NO_2^+ may be considered, at least to a first approximation, to agree with the above conclusion since the 1:2 meta:para ratio is the same for Cl_2 and "Cl^+," and the slight variation observed with NO_2^+ is probably not much greater than the uncertainties in the measurements.[30]

Medium Effects. Although the above view may explain the fact that also in the case of the CN and NO_2 groups no selectivity increase is observed on going from a charged reagent to molecular chlorine, additional factors must play a role to cause the significant decrease in selectivity which is, in fact, found. A special rate-enhancing factor at the para position due to an inverse polarizability effect[31] under the conditions of molecular chlorination seems unlikely, since the observed meta and para reactivities fit a Hammett-type equation well. Also, varying contributions of a polarizability effect for the reagents Cl_2 and "Cl^+" would imply transition states in the two sets of conditions characterized by markedly different extents of bond formation, which is not suggested by the behavior of the CF_3 group (Table III).

The observed selectivity order is more likely to originate from an abnormal behavior of the CN and NO_2 groups under conditions used for "Cl^+" chlorination and for nitration as compared to molecular chlorination in aqueous acetic acid. In agreement with this view, to account for the 1:2 meta:para ratios found in the nitration of nitrobenzene and the Ag^+-catalyzed chlorination, unusually high ρ values of about -15 or higher are required, whereas the ρ values usually quoted for these reactions are about -6.[28] It is interesting that the relative deactivating effects of meta and para nitro groups in protodetriethylgermylation[18] show no evidence of markedly stronger deactivation for the para position. Also, the relative deactivating effects of meta and para cyano and nitro groups on the solvolysis of aryldimethylcarbinyl chlorides differ only by a factor of 3.4 (NO_2) and 2.7 (CN).[32] The latter two reactions should have selectivities not far from those of nitration and "Cl^+" chlorination.[28]

In our opinion one of the most important factors which may cause the observed behavior, under the conditions used for the reactions with the charged reagents, is to be found in the interactions (H bonding) of these groups, acting as n donors, with the very acidic solvents used in these reactions. These interactions would increase the electron-withdrawing power of CN and NO_2 groups and, consequently, their discrimination between the para and meta positions.

The possibility that H-bonded species are involved in the nitration of nitro compounds in aqueous sulfuric acid has been discussed by Gillespie and Miller[33] and further evidence for related phenomena has been reported in more recent studies. Thus, in the detritiation of 4-substituted 4′-tritiobiphenyls in trifluoroacetic acid[34] and in the addition of trifluoroacetic acid to 4-phenyl-1-butenes,[35] such groups as NO_2 and CN were found to display a deactivating effect significantly larger than that expected. Enhanced polar effects of CN and NO_2 were similarly observed in a recent study of ^{19}F nmr shielding parameters[36] and of ^{13}C nmr chemical shifts[37] in trifluoroacetic acid solution as compared to those observed in weakly protic or nonprotic solvents. It is noteworthy that the polar effect of the CF_3 group appeared to be solvent insensitive.[36]

As to other factors possibly affecting the orientation ratios for the CN and NO_2 groups, we may quote the Lewis acid–base interactions of the substituent with the catalyst (*i.e.*, Ag^+)[38] or the electrophilic species. There is also a possibility for a charge effect on the approach of charged species to the deactivated (electron-deficient) ring. Since conjugation of –R groups renders the para position more electron deficient than the meta position in the ground state, the former would be more subject to a charge effect. The trifluoromethyl group would also be subject to this effect; it is therefore tempting to interpret in this manner the slight increase in the 1:2 meta:para ratio observed in the nitration of benzotrifluoride as compared to the chlorination reactions.

The picture above drives us to the conclusion that the orientation and reactivity data obtained in reactions with molecular chlorine seem to provide a closer description of the electronic effects of unsaturated groups such as CN and NO_2 in their unperturbed states than the similar data obtained from the reactions with NO_2^+ or "Cl^+" under conditions in which the electronic properties of the substituents can be appreciably modified. Work is in progress in our laboratories to gather more detailed information on the influence of –I, –R substituents in electrophilic substitution reactions with charged species with special regard to medium effects.

Experimental Section

Materials. The isomeric chloro derivatives of benzonitrile, nitrobenzene, and benzotrifluoride were, with the exception of *m*-chlorobenzonitrile, reagent grade commercial products, the purity of which was checked by vpc. *m*-Chlorobenzonitrile, mp 40–41° (from light petroleum), was prepared by treatment of *m*-chlorobenzamide with P_2O_5. The radioactive chlorine samples were ob-

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(29) J. C. D. Brand and R. P. Paton, *J. Chem. Soc.*, 281 (1952).

(30) (a) G. A. Olah and S. J. Kuhn in "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Vol. III, part 2, Interscience, New York, N. Y., 1964, p 1467, report a value of 11 for the 1:2 meta:para ratio in the nitration of benzotrifluoride by nitronium tetrafluoroborate in sulfolane; (b) ref 23 reports a value of *ca.* 20 for the nitration of benzotrifluoride under the same conditions.

(31) See ref 4, p 81.

(32) See ref 28, p 87.

(33) R. J. Gillespie and D. J. Millen, *Quart. Rev., Chem. Soc.*, 2, 277 (1948).

(34) R. Baker, R. W. Bott, C. Eaborn, and P. M. Greasley, *J. Chem. Soc.*, 627 (1964).

(35) P. E. Peterson, D. M. Chevli, and K. A. Sipp, *J. Org. Chem.*, 33, 972 (1968).

(36) R. W. Taft, E. Price, I. R. Fox, K. K. Andersen, and G. T. Davies, *J. Amer. Chem. Soc.*, 85, 709 (1963).

(37) G. C. Levy, G. L. Nelson, and J. D. Cargioli, *J. Chem. Soc. D*, 506 (1971).

(38) J. Grundnes and P. Klaboe in "The Chemistry of the Cyano Group," Z. Rappoport, Ed., Interscience, London, 1970, p 133.

tained from the Radiochemical Centre (Amersham, England) and were used without purification.

A. **Determination of Isomeric Distributions.** A solution of the reactants was prepared in aqueous acetic acid (80%, by volume), the resulting concentrations being about 1 *M* in the aromatic substrate and *ca.* 0.65 *M* in chlorine. The solution (10 ml) was then mixed with a sample containing about 50 μCi of $^{36}Cl_2$ and a small amount of Cl^- (5%) as an impurity. The latter step was carried out by sealing together the ampoules of the reagents and breaking an internal glass seal, according to standard procedures. The resulting solution was allowed to stand in the dark at room temperature for periods from 8 weeks to 2 years. The reaction mixture was then added to about 200 mg of each of the three inactive monochloro derivatives of the aromatic substrate, and treated with a solution of sodium sulfite in order to remove the unreacted chlorine. The organic materials were extracted several times with petroleum ether (bp 30-60°); the combined organic layers were washed with a solution of inactive sodium chloride and finally dried over sodium sulfate. After removal of the solvent, the residue was analyzed by preparative gas chromatography, using separated glass traps directly inserted into the detector block of a Model B (or Model D) Fractovap (Carlo Erba, Milan) to collect the individual fractions. The separations were carried out in 6 mm i.d. stainless steel columns, with helium as the carrier gas, under the following conditions.

Chlorinated Products from Benzonitrile. A mixed column (1 m long), containing 7.4 g of diisodecyl phthalate modified Bentone 34 (20% w/w on Celite) and 5.6 g of diisodecyl phthalate (20% w/w on Celite), was used at 175°.

Chlorinated Products from Nitrobenzene. A mixed column (1.3 m long), containing 10.2 g of diisodecyl phthalate modified Bentone 34 (25% w/w on Chromosorb) and 8 g of diisodecyl phthalate (25% w/w on Chromosorb), was used at 150°.

Chlorinated Products from Benzotrifluoride. An 8 m long column packed with tricresyl phosphate (25% w/w on Chromosorb W), was used at 150°.

The radioactivities of the purified fractions collected at the outlet of the gas chromatograph were measured with a Mark I Nuclear Chicago scintillation spectrometer, and the gas chromatographic purification was repeated until a constant value for the specific activity of each product was reached.

Because of the low conversion, it is possible that radiation damage produced within the reaction mixture by the tracers could promote radiolytic processes, responsible to some extent for the formation of the labeled chlorobenzonitriles. A rough calculation, however, shows that this is not the case, since the dose received by the system is, at most, 3000 rads. At this level of radiation damage, taking into account the dilution of the active chlorine, only a chain process with an exceedingly high energetic yield could contribute significantly to the observed yields.

B. **Competitive Experiments. (i) Relative Chlorination Rates of Benzonitrile and Benzotrifluoride.** Solutions containing benzonitrile (*ca.* 0.87 *M*), benzotrifluoride (*ca.* 0.19 *M*), and $^{36}Cl_2$ were prepared as previously described. After being allowed to stand for several weeks, the reaction mixture was added to known amounts of each of the six monochloro derivatives of the two aromatic substrates, and treated in the usual way. The residue was analyzed by preparative gas chromatography, using a 6 mm i.d. column (3 m long) packed with Apiezon L grease, 25% w/w on silanized Chromosorb W, with helium as the carrier gas. The temperature was kept at 140° until the benzonitrile peak emerged, then raised to 220° at a rate of 44° per min. In this way, separate fractions were obtained, containing the isomeric chlorobenzonitriles and chlorobenzotrifluorides, respectively. Relative rates of chlorination were determined by the radioactivities of these two fractions, allowance being made for the different initial concentrations of the two substrates.

(ii) Relative Chlorination Rates of Benzonitrile and Nitrobenzene. Solutions containing benzonitrile (*ca.* 0.24 *M*), nitrobenzene (*ca.* 0.91 *M*), and $^{36}Cl_2$ were prepared and treated as above, using the same column. The temperature was kept at 150° until the nitrobenzene peak emerged, then raised to 220° at the rate of 44° per min. Two fractions were obtained containing the isomeric chloronitrobenzenes and chlorobenzonitriles, respectively. Relative rates of chlorination were calculated as before.

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Reversible Hydrogen Abstraction. The Mechanism of Trichlorovinylation

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Abstract: The mechanism of the reaction of tetrachloroethylene with *n*-hexane and cyclohexane has been reinvestigated. The reaction has been shown to proceed by a free-radical chain mechanism involving reversible hydrogen abstraction by atomic chlorine as the product-determining process. The anomalous results obtained by comparing the isomer distributions for chlorination and chlorovinylation reactions have been accounted for by the differences in the chain-transfer rates of the alkyl radicals with molecular chlorine on the one hand, and tetrachloroethylene and hydrogen chloride on the other. The chlorination of cyclohexane with carbon tetrachloride was found, unlike the chlorovinylation reaction, to proceed without detectable reversal of the radicals formed during the reaction with the chloroform produced in the reaction.

The peroxide-initiated reaction of polychloroethylenes (Ia, b, and c) with various saturated hydrocarbons was reported by Schmerling and West[3] to give chlorovinylated alkanes. These authors proposed a free-radical chain mechanism which involves the chlorine atom as the chain-carrying species (Scheme I).

The mechanism, which involves a β scission of the carbon–chlorine bond (eq 2) and a product-determining abstraction of an alkyl hydrogen by atomic chlorine (eq 3), would predict that the final distribution of chlorovinylated products would be determined by the selectivity of atomic chlorine. Rust and Bell[4] have recently reported their investigation of the free-radical chlorovinylation of *n*-hexane using compounds

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[3] L. Schmerling and J. P. West, *J. Amer. Chem. Soc.*, 71, 2015 (1949).

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