

The Role of Copper Chlorides in the Sandmeyer and Meerwein Reactions

S. CARLTON DICKERMAN, DEREK J. DESOUZA, AND NORMAN JACOBSON

Department of Chemistry, New York University, University Heights, New York, New York 10453

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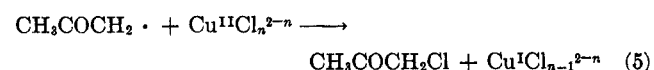
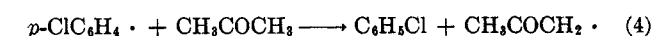
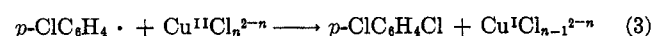
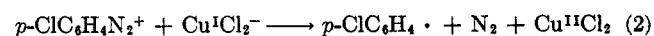
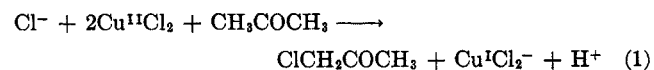
The mechanism of the Meerwein reaction of *p*-chlorobenzediazonium chloride with several monomers has been studied by determining the variation in the composition of the products of these reactions with initial concentration of cupric chloride. The results are inexplicable in terms of mechanisms for the Meerwein reaction that involve complexes of monomer with either cuprous or cupric chloride but are consistent with a three-way competition for a common intermediate, the *p*-chlorophenyl radical. Relative reactivities for the addition of this radical to the several monomers have also been measured.

In 1939, Meerwein, Buchner, and von Emster reported that the addition of aryldiazonium salts to acetone solutions of cupric chloride and monomer resulted in chloroarylation of the double bond.¹ Some of the diazonium salt is converted into the corresponding aryl chloride and arene and, in the absence of monomer, these two compounds are the major products of reaction. Since acetone solutions of cupric chloride have been shown to yield cuprous chloride (eq 1), the formation of aryl chloride represents a special case of the Sandmeyer reaction while in the presence of monomer the resulting transformation has become known as the Meerwein reaction. Although the mechanisms of these reactions have been investigated in several laboratories, "complex" mechanisms for the Meerwein reaction, which involve reactive complexes of monomer with cuprous and/or cupric chloride, were neither substantiated nor rigorously eliminated.² Since olefins do form complexes with cuprous chloride the former mechanism, in particular, has always appeared intuitively attractive. In 1961 Schrauzer reported that acrylonitrile forms complexes with both cuprous and cupric chloride as well as a biscomplex with nickel.³ The nickel complex was shown to yield Meerwein adduct when treated with *p*-chlorobenzediazonium chloride and Schrauzer suggested a mechanism for the Meerwein reaction involving a cage reaction between diazonium cation and π complex of monomer and cuprous chloride, *vide infra*. These findings obviously enhance the credibility of a "complex" mechanism for this reaction and have been cited by others in this connection.^{4,5} Our interest in ascertaining the role of complexes in the Meerwein reaction was twofold. First, it presented an interesting problem with respect to the design of experiments and, second, the results of competitive Meerwein reactions cannot be interpreted with any assurance in the absence of such information.⁶

p-Chlorobenzediazonium chloride was selected for this study and the products of the Sandmeyer reaction and four different Meerwein reactions were determined by glpc. These reactions were accomplished in 80% acetone-water at four different initial concentrations of cupric chloride, all at the same total chloride ion concentration. These data are presented in Table I. In every instance an increase in the initial concentration of cupric chloride is accompanied by increased formation of *p*-dichlorobenzene at the expense of chlorobenzene or chlorobenzene and Meerwein adduct.⁷ At each of the four cupric chloride concentrations the addition of acrylonitrile, methyl acrylate, methyl methacrylate, or styrene leads to a reduction in the amounts of both *p*-dichlorobenzene and chlorobenzene.

The molar ratios of *p*-dichlorobenzene/chlorobenzene, Sandmeyer/abstraction product, or S/A, in the presence and absence of monomer, are listed in Table II. Examination of these data reveals that this ratio is essentially independent of the presence of monomer. This finding confirms the existence of a common intermediate in the formation of these compounds and, in conjunction with earlier observations, permits the mechanistic description given below for this type of Sandmeyer reaction.

Mechanism of the Sandmeyer Reaction in Aqueous Acetone (eq 1-5).—Catalytic amounts of cuprous



chloride are effective and are produced from cupric chloride and acetone (eq 1) in a reaction originally reported in 1904 and rediscovered by Kochi⁸ and by Dickerman and coworkers.⁹ The reducing agent in eq 2 is formulated as the dichlorocuprate(I) anion in

(1) H. Meerwein, E. Buchner, and K. von Emster, *J. Prakt. Chem.*, **152**, 237 (1939).

(2) The mechanism and other aspects of these reactions have been reviewed by H. Zollinger in "Diazo and Azo Chemistry," Wiley-Interscience Publishers, New York, N. Y., 1961, pp 162-168, and by C. S. Rondstvedt, Jr., *Org. Reactions*, **11**, 189 (1960). Only those references in the earlier literature that bear directly on the present discussion will be cited here.

(3) G. N. Schrauzer, *Ber.*, **94**, 1891 (1961).

(4) L. F. Fieser and M. Fieser, "Topics in Organic Chemistry," Rheinhold Publishing Co., New York, N. Y., 1963, p 528.

(5) M. Rosenblum, W. G. Howells, A. K. Banerjee, and C. Bennett, *J. Amer. Chem. Soc.*, **84**, 2726 (1962).

(6) S. C. Dickerman, I. S. Megna, and M. M. Skoultchi, *ibid.*, **81**, 2270 (1959).

(7) The observation that the yield of Meerwein adduct from acrylonitrile is inversely related to the concentration of cupric chloride has been made previously but the fate of that part of the diazonium salt that does not yield adduct was not determined: J. K. Kochi, *ibid.*, **78**, 1228 (1956).

(8) J. K. Kochi, *ibid.*, **77**, 5274 (1955).

(9) S. C. Dickerman, K. Weiss, and A. K. Ingberman, *J. Org. Chem.*, **21**, 380 (1956); *J. Amer. Chem. Soc.*, **80**, 1904 (1958).

TABLE I
PRODUCTS OF THE SANDMEYER AND SEVERAL MEERWEIN REACTIONS OF *p*-CHLORO BENZENEDIAZONIUM CATION AS A FUNCTION OF INITIAL CUPRIC CHLORIDE CONCENTRATION^a

[CuCl ₂], M × 10 ³	Monomer	<i>p</i> -Dichlorobenzene (S)	Chlorobenzene (A)	Meerwein adduct (MCl)
5		34.0 ± 0.8	52 ± 1	
10		51 ± 1	35 ± 1	
50		76 ± 2	9.6 ± 0.5	
90		76 ± 3	7.2 ± 0.6	
5	AN	9.0 ± 0.2	10.7 ± 0.4	78 ± 1
10	AN	17.2 ± 0.5	10.0 ± 0.3	69 ± 1
50	AN	55.8 ± 0.5	5.0 ± 0.1	34 ± 1
90	AN	61 ± 3	4.0 ± 0.2	27.8 ± 0.7
5	MA	9.4 ± 0.4	13.6 ± 0.5	62 ± 3
10	MA	16.8 ± 0.4	11.7 ± 0.8	65 ± 3
50	MA	49.8 ± 0.2	6.8 ± 0.4	33.3 ± 0.2
90	MA	58 ± 1	5.3 ± 0.3	28.7 ± 0.7
5	MMA	6.42 ± 0.06	8.57 ± 0.02	72 ± 1
10	MMA	12.0 ± 0.3	8.1 ± 0.2	69.5 ± 0.0
50	MMA	44.8 ± 0.5	4.66 ± 0.08	39.7 ± 0.4
90	MMA	52.6 ± 0.8	3.76 ± 0.08	31.6 ± 0.4
5	St	12.0 ± 0.3	19.2 ± 0.4	67.3 ± 0.2
10	St	21.3 ± 0.2	17.2 ± 0.4	60.4 ± 0.4
50	St	54 ± 1	7.2 ± 0.2	28.2 ± 0.3
90	St	58.9 ± 0.6	5.51 ± 0.09	22.9 ± 0.3

^a At 30° from 10 mmol of diazotized *p*-chloroaniline, 48 mmol of chloride ion, the amount of cupric chloride tabulated, with and without the various monomers in solutions prepared from 80 ml of acetone and 20 ml of water. The following amounts of monomer were employed: 30 mmol of acrylonitrile (AN), 30 mmol of methyl acrylate (MA), 25.8 mmol of methyl methacrylate (MMA), and 10 mmol of styrene (St). For details, consult the Experimental Section. The deviations represent the reproducibility of three to seven determinations.

TABLE II
EFFECT OF SEVERAL MONOMERS ON THE RATIO OF *p*-DICHLOROBENZENE/CHLOROBENZENE (S/A) IN SANDMEYER AND MEERWEIN REACTIONS OF *p*-CHLORO BENZENEDIAZONIUM CATION^a

Monomer	S/A			
	5 ^b	10 ^b	50 ^b	90 ^b
None	0.65	1.5	7.9	11
Acrylonitrile	0.84	1.7	11	15
Methyl acrylate	0.69	1.4	7.3	11
Methyl methacrylate	0.75	1.5	9.6	14
Styrene	0.62	1.2	7.5	11

^a Calculated from the data in Table I. ^b [CuCl₂] × 10³.

accord with the observation that the rate of evolution of nitrogen from a diazonium salt is inversely related to the concentration of chloride ion¹⁰ and for reasons of logic. Thus, if the loss of nitrogen is essentially concurrent with electron transfer, the aryl radical must be generated in a solvent cage with CuCl₂.¹¹ These two species cannot exhibit any pronounced tendency for reaction as evidenced by the high proportion of radicals that escape the cage.¹² Since higher complexes of cupric chloride and chloride ion are very effective agents for oxidative-reductive ligand transfer¹³ (eq 3), it follows that the reducing agent in eq 2 cannot be formulated as CuCl₄³⁻ or CuCl₃²⁻ with any reasonable expectation that these reactions would produce a

(10) W. A. Cowdrey and D. S. Davies, *J. Chem. Soc.*, S48 (1949). For identical observations and a somewhat different interpretation, see E. Pfeil and O. Velten, *Ann. Chem.*, **562**, 163 (1949); **565**, 183 (1949).

(11) There does not appear to be any evidence for the independent existence of arylazo radicals.

(12) Obviously, the cage reaction is not an effective route to aryl chloride. For evidence for this type of reaction in water, see D. C. Nonhebel and W. A. Waters, *Proc. Roy. Soc. Ser. A*, **247**, 16 (1957).

(13) J. K. Kochi, *J. Amer. Chem. Soc.*, **79**, 2942 (1957), and earlier references cited therein.

significant yield of free aryl radicals. In other words the generation of aryl radicals in homogeneous Sandmeyer reactions appears to depend on the fact that CuCl₂⁻ is by far the most effective reducing agent in such systems. Although the bulk of evidence for formulating the intermediate as an aryl radical will be presented after consideration of the Meerwein reaction, it is appropriate at this point to cite several observations that support reactions 4 and 5 in this mechanism. These include the facts that abstraction from acetone is a characteristic reaction of phenyl radicals,¹⁴ that 9-acetonylanthracene is a product of the decomposition of *N*-nitrosoacetanilide in acetone solutions of anthracene,¹⁵ and that there is a one to one correspondence in yields of aryl chloride and chloroacetone.⁹

The molar ratios of Meerwein adduct/chlorobenzene, MCl/A, for the reactions of acrylonitrile, methyl acrylate, methyl methacrylate, and styrene at the four different initial concentrations of cupric chloride are given in Table III. An examination of these data

TABLE III
RATIOS OF MEERWEIN ADDUCT/CHLOROBENZENE (MCl/A) IN SEVERAL MEERWEIN REACTIONS OF *p*-CHLORO BENZENEDIAZONIUM CATION AS A FUNCTION OF INITIAL CUPRIC CHLORIDE CONCENTRATION

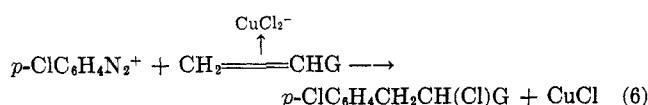
Cupric chloride, mol/l. × 10 ³	MCl/A ^a			
	AN	MA	MMA	St
5	7.3	4.6	8.4	3.5
10	6.9	5.6	8.6	3.5
50	6.8	4.9	8.5	3.9
90	7.0	5.4	8.4	4.2

^a Calculated from the data in Table I for acrylonitrile (AN), methyl acrylate (MA), methyl methacrylate (MMA), and styrene (St).

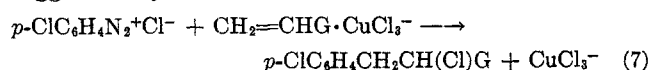
(14) R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963).

(15) N. Milstein, unpublished results.

reveals that the ratio of MCl/A , for each of the monomers, is independent of cupric chloride concentrations.¹⁶ Therefore, the conclusion that formation of Meerwein adduct and chlorobenzene is associated with a common intermediate appears inescapable. Neither of the "complex" mechanisms which have been proposed for the Meerwein reaction is consistent with these findings. Thus, the cuprous chloride-complex mechanism, suggested by Schrauzer³ and reproduced below in eq 6, demands that the ratio of Meerwein adduct to combined amounts of *p*-dichlorobenzene and chlorobenzene should remain constant as cupric and thus cuprous



chloride is varied (eq 1). In other words the relative rates of two competing reactions of the same order in a reactant are not altered by a change in the concentration of that reactant. Consideration of the cupric chloride-complex mechanism (eq 7), suggested by Rondestvedt and Vogel,¹⁷ is somewhat



more complicated in that *p*-dichlorobenzene and chlorobenzene are presumed to arise from a cuprous chloride initiated decomposition of the diazonium cation while Meerwein adduct is formed from this cation and a complex of monomer and cupric chloride. However, it has been observed that an increase in the concentration of cupric ion does not produce a corresponding increase in the concentration of cuprous ion (eq 1).⁷ Therefore, this mechanism requires that formation of Meerwein adduct should at least parallel any increase in cupric chloride concentration. Again, this is not observed and one is forced to conclude that complexes of monomer with both cuprous and cupric chloride are mechanistically unimportant in Meerwein reactions accomplished under the reaction conditions described here.¹⁸ However, these experiments represent typical Meerwein reactions and were selected such that any conclusions would have some generality.

It is now obvious that the formation of *p*-dichlorobenzene, chlorobenzene, and Meerwein adducts represents a three-way competition for the same intermediate. Furthermore this intermediate reacts with chlorobenzene,¹⁹ nitrobenzene,¹⁹ and anthracene,^{20,21} naphthalene,²⁰ phenanthrene,²² biphenylene,²³ pyrene,²⁴ and

(16) Presumably the same kind of information could have been obtained by holding cupric chloride constant and varying the acetone concentration. However, the abstraction reaction is rather insensitive and such a procedure would have necessitated drastic changes in the medium with concurrent problems.

(17) C. S. Rondestvedt, Jr., and O. Vogel, *J. Amer. Chem. Soc.*, **77**, 2313 (1955); **77**, 3067 (1955).

(18) Complexes which possess a low order of reactivity with the diazonium cation are not excluded and such species may be responsible for the small effects of monomer on the rate of evolution of nitrogen, although there are other interpretations.

(19) S. C. Dickerman and K. Weiss, *J. Org. Chem.*, **22**, 1070 (1957).

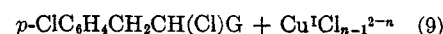
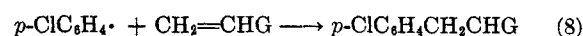
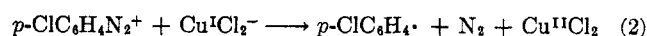
(20) S. C. Dickerman and G. B. Vermont, *J. Amer. Chem. Soc.*, **84**, 4150 (1962).

(21) S. C. Dickerman, A. M. Felix, and L. B. Levy, *J. Org. Chem.*, **29**, 26 (1964).

(22) S. C. Dickerman and I. Zimmerman, *J. Amer. Chem. Soc.*, **86**, 5048 (1964).

(23) S. C. Dickerman, N. Milstein, and J. F. W. McOmie, *ibid.*, **87**, 5521 (1964).

benzene^{19,20,22-24} to yield aryl derivatives. For chlorobenzene and nitrobenzene the substitution pattern is very similar to that produced in the Gomberg-Bachmann reaction or by the decomposition of aroyl peroxide. For the polycyclic aromatic hydrocarbons the Meerwein method of arylation gives partial rate factors that are essentially identical with those obtained by decomposing *N*-nitrosoacetanilide in benzene solutions of arene.²⁵ At low cupric concentrations the intermediate also initiates polymerization.¹² This mass of evidence indicates that the intermediate common to both the Sandmeyer and Meerwein reactions is the free aryl radical²⁶ and that the mechanism of the latter reaction must be formulated as indicated in the accompanying equations. This is the same mechanism that was first proposed in 1956 as the simplest inter-



pretation of the available evidence.⁹ Although Kochi originally suggested the possibility of a "complex" mechanism,⁷ his later proposal is essentially that given here.¹³

Since abstraction from acetone and addition to monomer represent competing reactions of the *p*-chlorophenyl radical, the rate of addition relative to abstraction for each monomer may be calculated by the

$$k_M/k_A = \frac{[\text{acetone}] 2.3 \log \frac{[M_0]}{[M_0] - [M]}}{[\text{chlorobenzene}]}$$

accompanying expression. These ratios, at the four cupric chloride concentrations, are given in Table IV.

TABLE IV
RATE CONSTANTS FOR THE ADDITION OF
THE *p*-CHLOROPHENYL RADICAL TO SEVERAL MONOMERS,
RELATIVE TO ABSTRACTION FROM ACETONE AND
TO ADDITION TO ACRYLONITRILE, AS A FUNCTION OF
INITIAL CUPRIC CHLORIDE CONCENTRATION

Cupric chloride, mol/l. $\times 10^3$	k_M/k_A^a			
	AN	MA	MMA	St
5	307	185	416	635
10	285	227	428	587
50	262	186	393	502
90	266	207	387	515
	$(k_M/k_A)_{av}$			
	280 \pm 15	202 \pm 16	406 \pm 16	558 \pm 51
	k_M/k_{AN}			
	1	0.72	1.4	2.0
	k_M/k_{AN}^b			
	1	0.88	1.4	1.8

^a Calculated by the expression in the text for acrylonitrile (AN), methyl acrylate (MA), methyl methacrylate (MMA), and styrene (St). ^b Found by direct competition; see text.

(24) S. C. Dickerman and W. F. Feigenbaum, Third Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa., Feb 1968, p 66.

(25) Similar orientation or, preferably, partial rate factors from different sources constitutes good evidence for the identity of the attacking species. However, the converse line of reasoning is less secure in view of the fact that the process of homolytic aromatic substitution requires an aromatizing agent.

(26) Alternative explanations include complexes of the aryl radical with arene, cupric chloride, acetone, and water. However, a complex of the first type and one of the others would have to possess almost identical reactivity and this appears highly fortuitous.

The k_M/k_A ratio for each monomer should be independent of the initial concentration of cupric chloride and this appears to be so within the accuracy of these experiments. These ratios are all relative to the same reaction and therefore may be set relative to one another. This was done using the average values of the ratios and the next to last row in Table IV represents the reactivities of the several monomers for addition of the *p*-chlorophenyl radical, all relative to acrylonitrile. The sequence of reactivity, styrene > methyl methacrylate > acrylonitrile > methyl acrylate, as well as the magnitude of the individual numbers, is in good agreement with the data obtained in direct competition, the last row of Table IV.²⁷ These and similar findings for other aryl radicals will be discussed in this paper.

Experimental Section

Materials.—Acetone (J. T. Baker Co., Baker Analyzed), biphenyl (Eastman Kodak Co., 721), *p*-chloroaniline (Eastman Kodak Co., 505), chloroform (Baker Analyzed), cupric chloride dihydrate (Baker Analyzed), *p*-dichlorobenzene (Eastman Kodak Co., 89), lithium nitrite monohydrate (A. D. MacKay Co., reagent grade), lithium chloride (Fisher Scientific Co., Fisher Certified Reagent), phenanthrene (Eastman Kodak Co., 599), and anhydrous sodium sulfate (Baker Analyzed) were used as supplied. Acrylonitrile (Matheson Coleman and Bell, practical grade), chlorobenzene (Fisher Certified Reagent), *m*-chlorotoluene (Eastman Kodak Co., 2449), methyl acrylate (Matheson Coleman and Bell, practical grade), methyl methacrylate (Matheson Coleman and Bell, practical grade), and distilled water were redistilled before use. Prior to distillation the monomers were freed of inhibitor by extraction with dilute sodium hydroxide, etc., and after distillation were stored for short periods of time under nitrogen. Initially, the styrene (Eastman Kodak Co., 1465) was treated similarly and redistilled under nitrogen and reduced pressure; however, it was found that the elimination of the distillation step did not alter the results and this procedure was followed in some of the runs.

The Meerwein adducts of *p*-chlorobenzenediazonium chloride and acrylonitrile,²⁸ methyl methacrylate,²⁹ and styrene³⁰ have been described previously and were prepared by similar procedures. An authentic sample of *trans-p*-chlorostilbene was also synthesized from the styrene adduct.^{1,31} Methyl 2-chloro-3-*p*-chlorophenylpropanoate was prepared from methyl acrylate and diazotized *p*-chloroaniline by the standard procedure for the Meerwein reaction recommended by Rondstvedt³ and isolated as a colorless oil of bp 95° (0.4 mm).

Anal. Calcd for $C_{10}H_{10}Cl_2O_2$: C, 51.50; H, 4.62; Cl, 30.40. Found: C, 51.29; H, 5.37; Cl, 30.00.³²

Procedures.—The Sandmeyer and Meerwein reactions were performed in four single-necked, standard-taper erlenmeyer flasks fitted with pressure release stoppers and partially immersed in a constant-temperature bath at $30.0 \pm 0.5^\circ$. All of the solutions of reagents, except that containing the diazonium salt, were deoxygenated by passing nitrogen through them for about 30 min and were added under nitrogen. Each of the four flasks was charged with 80 ml of acetone and individually with the following solutions or reagents: flask 1, 1.00 ml of water and 9.00 ml of 1.00 *F* cupric chloride; flask 2, 2.50 ml of water, 5.00 ml of 1.00 *F* cupric chloride, and 2.50 ml 3.20 *F* lithium chloride; flask 3, 4.00 ml of water, 1.00 ml of 1.00 *F* cupric chloride, and 5.00 ml of 3.20 *F* lithium chloride; flask 4, 4.20 ml of water, 0.50 ml of 1.00 *F* cupric chloride, and 5.31 ml of 3.20 *F* lithium chloride. If required, 0.0100–0.300 mol of monomer was added at this point and the flasks were placed in the bath. After about 30 min, 10.0 ml of a solution of *p*-chlorobenzenediazonium chloride was added to each flask. This solution was prepared from 0.50 mol of *p*-chloroaniline, 25.0 ml of 6 *F* hydrochloric acid, and 3.56 g of lithium nitrite in 5 ml of water. After diazotization, the excess nitrous acid was destroyed with urea, the solution was diluted to 50 ml and filtered. The reactions were complete in from 3 to 4 hr as indicated by a negative test with 2-naphthol. At this point the reaction mixtures were diluted with 250 ml of water and extracted with four portions of chloroform. The combined extracts were dried over anhydrous sodium sulfate and the internal standards were added.

Analyses.—The products of these Sandmeyer and Meerwein reactions were analyzed by glpc using *m*-chlorotoluene as the internal standard for both chlorobenzene and *p*-dichlorobenzene. Biphenyl was used for this purpose for the Meerwein adducts except for that derived from styrene where phenanthrene was substituted. Some of the earlier analyses for chlorobenzene and *p*-dichlorobenzene and the adducts were made on Perkin-Elmer Model 154-C and F & M Model 500 gas chromatographs, respectively. The remainder were accomplished using an F & M Model 810 instrument with flame-ionization detector. These analyses were made with a pair of 6 ft \times 0 in. columns of copper tubing prepared with 10% w/w SE-30 on Chromosorb P.

In contrast to the other Meerwein adducts, which exhibited single peaks, that from styrene always gave a double response. The larger of these two peaks has the same retention time as an authentic sample of *trans-p*-chlorostilbene. Therefore, the smaller peak of shorter retention time has been assigned to the *cis* isomer. Since 1-*p*-chlorophenyl-2-chloro-2-phenylethane is not thermally stable for long periods of time at room temperature,³⁰ it is not surprising that this compound undergoes dehydrochlorination during analysis.

Registry No.—*p*-Chlorobenzenediazonium chloride, 2028-74-2; acrylonitrile, 107-13-1; methyl methacrylate, 80-62-6; styrene, 100-42-5; methyl acrylate, 96-33-3; chlorobenzene, 108-90-7; *p*-dichlorobenzene, 106-46-7; cupric chloride, 7447-39-4.

(32) These analyses were performed by the Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N. Y. 11377.

(27) S. C. Dickerman, D. J. DeSouza, M. Fryd, I. S. Megna, and M. M. Skoultchi, *J. Org. Chem.*, **34**, 714 (1969).

(28) W. H. Brunner and H. Berger, *Monatsh.*, **79**, 187 (1948).

(29) P. L'Ecuyer and C. A. Oliver, *Can. J. Res.*, **B28**, 648 (1950).

(30) J. K. Kochi, *J. Amer. Chem. Soc.*, **77**, 5090 (1955).

(31) W. Brunner and J. Kustascher, *Monatsh.*, **82**, 100 (1951).