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The Cleavage of Bonds by Low Valent Transition Metal Ions. The Homogeneous Reduction of Alkyl Halides by Chromous Sulfate

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The homogeneous reduction of alkyl halides by chromous sulfate in aqueous dimethylformamide leads to dimerization of the alkyl moiety or to the replacement of halogen by hydrogen. The stoichiometry, kinetics, stereochemistry, and the reactivities of the halides for both processes are in accord with a mechanism in which a free radical is generated in the initial scission of the carbon–halogen bond by Cr^{++}. The ultimate course of the reaction is dependent upon the nature of the radical. Paths for the dissipation of intermediate ions of the sort RCr^{++} are presented.

Introduction

Previous studies of the influence of strongly reducing low valent transition metal salts upon the course of reactions that proceed by way of polyarylmethyl cations have demonstrated that the metal ions are not oxidized, and indeed are innocuous, when halide ions are absent from the media. However, in the presence of halide, oxidation of the metal ion does occur and a dimer of the polyarylmethyl fragment is obtained exclusively.[1]

It was concluded from these findings that process 1 was unimportant, and it was suggested that the first step of the reductive coupling was the result of a direct

$$R^+ + M^{+n} \longrightarrow R\cdot + M^{+n+1} \qquad (1)$$

attack of the metal ion on the intermediate organic halide (2) to produce a free radical which subsequently dimerized. An alternate path (3) in which a halide complex of the metal ion did reduce the carbonium ion could not be rigorously eliminated.

$$RX + M^{+n} \longrightarrow R\cdot + MX^{+n} \qquad (2)$$

$$R^+ + MX^{+n} \longrightarrow R\cdot + MX^{+n+1} \qquad (3)$$

Although the cleavage of carbon–halogen bonds by low valent transition metal species has been advanced as a step in the mechanism of the coupling of Grignard reagents by catalytic amounts of transition metal halides[2] (principally $CuCl_2$, $FeCl_3$, $CoCl_2$, $CrCl_3$), and in the deoxygenation of epoxides by phenylmagnesium bromide in the presence of $FeCl_3$,[3] direct evidence for process 2 has been scanty. Thus, Conant and Lutz[4] observed the reduction of some α-haloketones by $TiCl_3$. A similar reduction of α-haloketosteroids by $CrCl_2$ and the dehalogenation of 5,6-dibromo-3-ketosteroids and 5,6-dibromosterols in aqueous acetone has been reported by Julian[5] and co-workers. Aqueous acidic solutions of chromous chloride are oxidized by carbon tetrachloride,[6a,b] chloroform,[6a,b] bromoethanol,[7] and bromoethylamine.[7] The coupling of 9-chloroacridine by chromous sulfate (acetate) in acetic acid[8] has been noted and, most interestingly, Anet has described the ions $Cl_2CHCr(H_2O)^{++}$ and $C_6H_5–CH_{21}Cr(H_2O)_5^{++}$ which result from the interaction of aqueous chromous perchlorate with chloroform[6b] and benzyl chloride.[9]

As a part of our studies of the cleavage of bonds by low valent transition metal species, we wish to present direct evidence for the occurrence of process 2 and to indicate the general scope and mechanism of the reduction of alkyl halides by low valent transition metal ions. Chromous sulfate in aqueous dimethylformamide was employed as the reductant throughout the present work because of the favorable solubility of alkyl halides in this media and the easy observance of a blue to green color change attendant upon the oxidation of chromous ion.

Results

Stoichiometry.—The results of the homogeneous reduction of a variety of alkyl halides by chromous sulfate in 50% aqueous dimethylformamide (DMF) are listed in Table I. The substrates are listed in a decreasing order of reactivity. The reactions were carried out at room temperature in a nitrogen atmosphere with initial concentrations of Cr^{++} ranging from 0.1 to 0.35 *M* and those of the halides from 0.02 to 0.05 *M* except where indicated.

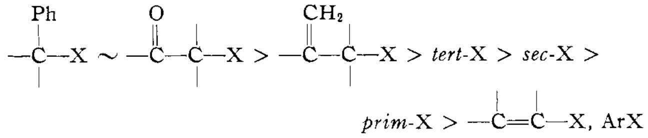
In addition to those substrates listed in Table I many halides were scanned for reactivity toward Cr^{++}. Under conditions in which the initial concentrations of Cr^{++} was 0.3 *M* and the halide was 0.2 *M*, the following halides reacted slowly: *sec*-butyl bromide, *n*-butyl bromide, isopropyl chloride, *n*-propyl chloride, and 1,4-dichlorobutane. The products and stoichiometry of these reactions were not ascertained. Under similar conditions, the following were inert (no perceptible color change after 3 days): phenyl chloride, phenyl bromide, phenyl iodide, α-bromonaphthalene, *cis*- and *trans*-1-chloropropene, and 2-chloropropene.

Thus, the reduction of alkyl halides by Cr^{++} in aqueous media results in two general transformations, replacement of halogen by hydrogen (4) ("total reduction") and coupling (5). It should be noted that the

$$RX + 2Cr^{++} + H^+ \longrightarrow RH + CrX^{++} + Cr^{+3} \qquad (4)$$

$$RX + Cr^{++} \longrightarrow {}^1/_2R_2 + CrX^{++}$$
$$CrX^{++} \longrightarrow Cr^{+3} + X^- \qquad (5)$$

inorganic ion resulting from the reduction of an alkyl chloride is the apple-green $CrCl^{++}$ and not the deeper green $CrSO_4^+$. The corresponding bromide complex ($CrBr^{++}$) is however much less stable[10] and could not be detected as a product from the reduction of an alkyl bromide. The reactivity of the monohalides to Cr^{++} fall then in the order



$$\text{—}\overset{\text{Ph}}{\underset{|}{\overset{|}{\text{C}}}}\text{—X} \sim \text{—}\overset{\text{O}}{\overset{\Vert}{\text{C}}}\text{—}\underset{|}{\overset{|}{\text{C}}}\text{—X} > \text{—}\overset{\text{CH}_2}{\overset{\Vert}{\text{C}}}\text{—}\underset{|}{\overset{|}{\text{C}}}\text{—X} > \textit{tert}\text{-X} > \textit{sec}\text{-X} > \textit{prim}\text{-X} > \text{—}\overset{|}{\text{C}}\text{=}\overset{|}{\text{C}}\text{—X, ArX}$$

The ease of cleavage of the different halogens from carbon is reflected in the relative rates of reduction of the allylic halides to propylene. These are in the order allyl iodide ∼ allyl bromide > allyl chloride in the approximate ratio of 4:4:1.

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[1] C. E. Castro, *J. Am. Chem. Soc.*, **83**, 3262 (1961).

[2] M. S. Kharasch and E. K. Fields, *ibid.*, **63**, 2316 (1941).

[3] M. S. Kharasch, L. Birtz, W. Nudenberg, A. Bhattacharya, and N. C. Yang, *ibid.*, **83**, 3229, 3232 (1961).

[4] J. B. Conant and R. E. Lutz, *ibid.*, **47**, 881 (1925); for a survey earlier related work see J. B. Conant and H. B. Cutter, *ibid.*, **48**, 1016 (1926).

[5] P. L. Julian, W. Cole, A. Magnani, and E. W. Meyer, *ibid.*, **67**, 1728 (1945).

[6] (a) T. Kiba and K. Terada, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **75**, 196 (1954); (b) F. A. L. Anet, *Can. J. Chem.*, **37**, 58 (1959).

[7] F. A. L. Anet and E. Isabelle, *ibid.*, **36**, 589 (1958).

[8] R. Royer, *J. Chem. Soc.*, 1663 (1949).

[9] F. A. L. Anet and E. Leblanc, *J. Am. Chem. Soc.*, **79**, 2649 (1957).

[10] J. H. Espenson and E. L. King, *J. Phys. Chem.*, **64**, 380 (1960).

TABLE I

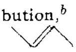
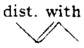
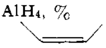
PRODUCTS OF THE REDUCTION OF ALKYL HALIDES BY Cr^{++}

Substrate	Cr^{++} stoichiometry	Conversion,[a] %	Product	Calcd. % yield[b]	Reactivity
Ethylene dibromide[c,d]	2	93	Ethylene	100	Rapid reaction complete in 5–30 min.
Methylene bromide[g]	4	97	Methane	101	
Benzhydryl bromide[h]	1	100	*sym*-Tetraphenylethane	90	
α-Phenylethyl bromide[d]	1	58	2,3-Diphenylbutane	94	
p-Bromphenacyl bromide[f]	2	91	*p*-Bromoacetophenone	96	
			1,2-Di-*p*-bromobenzoylethane	1	
α-Phenylethyl chloride[d]	1	96	2,3-Diphenylbutane	98	Moderate reaction complete in 1–3 hr.
Phenacyl chloride[f]	2	79	Acetophenone	99	
Allyl iodide	(2)[e]		Propylene		
Allyl bromide	2	100	Propylene	98	
Allyl chloride	2	72	Propylene	98	
cis-1,3-Dichloropropene	4	94	Propylene	102	
trans-1,3-Dichloropropene	4	95	Propylene	103	
t-Butyl bromide	(2)[e]		Isobutane		
Isopropyl bromide	2	31	Propane	99	Slow reaction requiring 1–3 days to the conversion indicated
n-Propyl bromide	2	25	Propane	104	
β-Phenylethyl bromide	2	22	Ethylbenzene	96	
1,4-Dibromobutane	(4)[e]		*n*-Butane		

[a] Conversion to the product indicated. [b] Yields are based upon the Cr^{++} stoichiometry indicated; all yields are quantitative within the experimental error. [c] Taken from data of ref. 1; solvent, aqueous acetone. [d] The ratio of the initial concentration of Cr^{++} to halide was 1:3 with initial halide at 0.1 *M*. [e] The stoichiometry is inferred in these cases; *cf.* the Experimental section. [f] The solvent was 2:1 DMF–H_2O. [g] The solvent was 1:2 DMF–H_2O. [h] Taken from ref. 1.

TABLE II

PRODUCTS OF THE REDUCTION OF THE BUTENYL CHLORIDES BY $CrSO_4$ AND $LiAlH_4$

Substrate	Cr^{++} stoichiometry	Conversion, %	Calcd. % yield[a] C_4H_8	Distribution,[b] % 			Product dist. with $LiAlH_4$, % 		
cis-Crotyl Cl	2	86	103	95.9	1.1	3.0	..	4.8	95.2
trans-Crotyl Cl	2	79	95	94.8	1.3	3.9	..	98.6	1.4[c]
Crotyl Cl mix	2	93	104	95.5	1.0	3.5	..	71.0	29.0
3-Chlorobutene-1	2	83	105	95.5	1.1	3.4	61.3	30.2	8.5

[a] All yields are quantitative within experimental error. [b] The isomer distributions are identical within experimental error. [c] A trace of *n*-butane was also present.

The very rapid reduction of methylene bromide (6) and ethylene dibromide (7) is in sharp contrast to

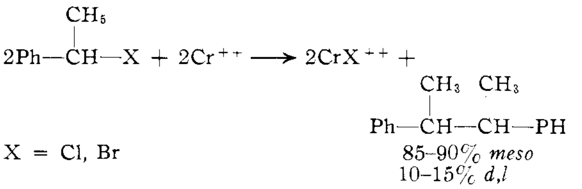
$$CH_2Br_2 + 4Cr^{++} + 2H^+ \longrightarrow CH_4 + 2CrBr^{++} + Cr^{+3} \quad (6)$$

$$Br\text{-}CH_2\text{-}CH_2\text{-}Br + 2Cr^{++} \longrightarrow 2CrBr^{++} + CH_2{=}CH_2 \quad (7)$$

the quite slow reductions of unactivated primary bromides. A description of the reduction of multiple halides of this sort will be reported separately. They are included in the present work only to indicate the scope of these reactions.

Kinetics.—Allyl chloride and α-phenylethyl chloride were selected for kinetic study as typical cases of the reduction (4) and of the coupling reaction (5), respectively. The over-all order of the reduction of allyl chloride by Cr^{++} was calculated to be 1.98 from a plot of Cr^{++} concentration *vs.* time by employing the fractional life method.[11] Rate constants were evaluated graphically by plotting the expressions $1/(a - 2x) = k_2t + (1/a)$ when stoichiometric ratios of initial concentrations were employed, and $\log (a - 2x)/(b - x) = k_2t(a - 2b)/(2.303) + \log (b/a)$. In both expressions $a = (Cr^{++})_0$ and $b = (RCl)_0$. Good straight line plots were obtained through 95% completion of the reaction, and in 1:1 DMF–H_2O solutions that were 1.0 *F* in $HClO_4$, $k_2^{29.7} = 1.2 \pm 0.1$ l./mole/min. For the α-phenylethyl chloride coupling, the typical second-order expressions for equivalent and nonequivalent initial concentrations were plotted. Again, good linearity was obtained but successive runs were not as reproducible as they were for allyl chloride because of the rapidity of the reaction at the relatively high (~0.15 *M*) concentrations that were necessary. In 1:1 DMF–H_2O solutions that were 1.1 *F* in $HClO_4$, $k_2^{29.7} = 2.3 \pm 0.8$ l./mole/min. At low initial concentrations (~0.01 *M*), with 1:1 ratios of Cr^{++} to α-phenylethyl chloride, competing solvolysis of the halide occurred and Cr^{++} consumption was greatly retarded after a few minutes.

Stereochemistry.—The stereochemistry of the coupling process is illustrated by the conversion of both optically inactive α-phenylethyl chloride and α-phenylethyl bromide to the same distribution of the enantiomorphic diphenylbutanes (8)



$$2Ph\text{—}\underset{}{\overset{CH_5}{\overset{|}{C}}}H\text{—}X + 2Cr^{++} \longrightarrow 2CrX^{++} + Ph\text{—}\overset{CH_3}{\overset{|}{C}}H\text{—}\overset{CH_3}{C}H\text{—}PH \quad (8)$$

X = Cl, Br

85–90% *meso*
10–15% *d,l*

The allylic butenyl chlorides were chosen to delineate the stereochemical course of the replacement of halogen by hydrogen. These chlorides were reduced with $LiAlH_4$ in tetrahydrofuran and with chromous sulfate in 50% aqueous dimethylformamide at room temperature. The product distribution of the butenes obtained from the $LiAlH_4$ reduction of *cis*- and *trans*-crotyl chloride can be taken as an assay of the stereochemical purity of these substances.[12a] However, in accord with the "abnormal SN2" reduction of other secondary allylic chlorides[13] with $LiAlH_4$, the reduction

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(11) A. Frost and R. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 40.

(12) (a) L. D. Huestis and L. J. Andrews, *J. Am. Chem. Soc.*, **83**, 1964 (1961); (b) L. F. Hatch and S. S. Nesbit, *ibid.*, **72**, 727 (1950).

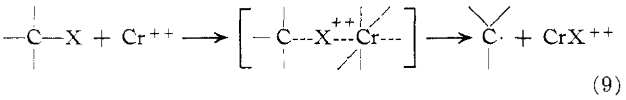
(13) L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *ibid.*, **81**, 5944 (1959), and references therein.

of 3-chlorobutene-1 by this reagent does proceed with some bond migration and isomerization. The results of these reactions are summarized in Table II.

The Cr^{++} reduction of these halides proceeded at approximately the same rate. With initial concentrations of 0.24 *M* Cr^{++} and 0.03 *M* C_4H_8Cl, the reaction was 70% complete (butene evolution) in 5 min. Moreover, it was demonstrated by separate experiments that none of the isomeric butenes are interconverted upon long exposure (1 day) to reaction conditions. Similarly, as would be expected,[14] the isomeric chlorides were not found to equilibrate in either dimethylformamide or aqueous dimethylformamide after 4 hr. at room temperature.

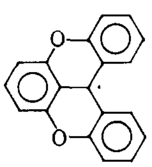
Discussion

The Initial Cleavage.—We believe that the reactivity sequence,[15] kinetics, and stereochemistry presented in the foregoing section show clearly that the initial and rate-determining step in these reductions is the attack of the metal ion on the alkyl halide. This results in the transfer of a halogen atom from carbon to chromium and the production of a free alkyl radical (9). This initial step and its transition state are entirely analogous



$$-\overset{|}{\underset{|}{C}}-X + Cr^{++} \longrightarrow \left[-\overset{|}{\underset{|}{C}}\text{---}\overset{++}{X}\text{---}\overset{|\,/}{\underset{/\,|}{Cr}}\text{---} \right] \longrightarrow \overset{\diagdown\,\diagup}{\underset{|}{C}}\cdot + CrX^{++} \qquad (9)$$

to the processes thoroughly described by Taube for the reduction of inorganic ions like $Cr(NH_3)_5Cl^{++}$ and $Co(NH_3)_5Cl^{++}$ [16] by Cr^{++}. That a carbon free radical· can result from such interaction is evidenced by the isolation of the highly hindered



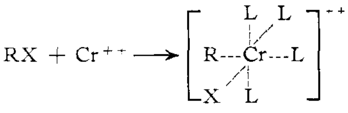
upon treatment of the corresponding chloride with acidic chromous chloride in acetic acid.[17] The ultimate course of the reduction of alkyl halides by Cr^{++} is a function of the stability of the generated alkyl radical as manifested in its propensity to dimerize or be scavenged by Cr^{++} (10).

$$\begin{tikzcd} R\cdot \arrow[r] \arrow[dr, "Cr^{++}/H^{+}"] & \tfrac{1}{2}R_2 \\ & RH + Cr^{+3} \end{tikzcd} \qquad (10)$$

The Reductive Dimerization.—The simplest mechanism of the coupling reaction (5) consistent with the findings of the present study is

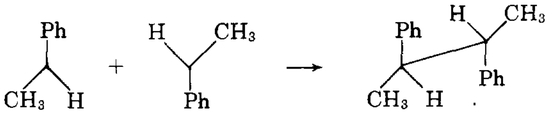
$$RX + Cr^{++} \longrightarrow R\cdot + CrX^{++} \qquad (11)$$
$$2R\cdot \longrightarrow R_2$$

It remains open, however, whether the radical produced is entirely free as depicted above or loosely affiliated with the metal ion (12) and whether the ions present influence the dimerization process.[18]



$$RX + Cr^{++} \longrightarrow \left[\begin{array}{c} L\quad L \\ R\text{---}Cr\text{---}L \\ X\quad L \end{array} \right]^{++} \qquad (12)$$

The high proportion of *meso*-2,3-diphenylbutane obtained from the coupling of the α-phenylethyl halide bespeaks a process in which a randomized free radical attacks another of its kind in the most comfortable



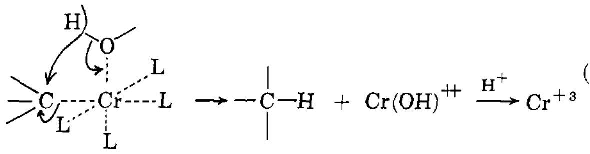
steric arrangement or attacks a rapidly and reversibly forming metal ion complex (15) in a similar fashion.[19]

$$\begin{tikzcd} RCr^{++} \arrow[r, shift left] \arrow[d, "R\cdot"] & R\cdot + Cr^{++} \arrow[l, shift left] \arrow[d, "R\cdot"] \\ R_2 + Cr^{++} & R_2 \end{tikzcd} \qquad (15)$$

The Total Reduction.—Because of the steric results of the butenyl chloride reductions, we prefer the sequence (9) followed by (16)[20] as the first steps in these

$$RX + Cr^{++} \longrightarrow R\cdot + CrX^{++} \qquad (9)$$
$$R\cdot + Cr^{++} \longrightarrow RCr^{++} \qquad (16)$$

reactions. In these cases, the relatively high concentration of Cr^{++} to alkyl halide and the instability of the alkyl radicals that might result from the reversal of (16) afford an intermediate RCr^{++} the opportunity to cleave in another way. We believe the heterolytic scission of a complex RCr^{++} is the transformation that leads to alkane and that it is best described as a synchronous process in which a proton is transferred from the solvation sphere of the metal ion to the incipient carbanion (17).[21]



(17)

For allylic radicals, the geometry for proton transfer from the metal ion is ideal (18). Moreover, although the thermodynamic distribution of the butenes[22] at room temperature is 77% *trans*-butene-2, 21% *cis*-, and 2% butene-1, upon reduction with Cr^{++}, the allylic butenyl chlorides yield predominantly the least stable butene-1. Similarly, both *cis*- and *trans*-1,3-dichloropropene are reduced to propylene by way of the terminal

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[14] The relatively slow rates of equilibration of allylic bromides in warm *n*-decane are reported in ref. 13.

[15] The sequence is quite analogous to that recently noted for the reduction of alkyl halides by R_3SnH in which an initial scission to radicals is proposed: H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3585 (1962).

[16] H. Taube in "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, edited by H. J. Emeléus and A. G. Sharpe, Academic Press, Inc., New York, N. Y., 1959, Chapter 1, and references therein.

[17] O. Neunhoeffer and H. Haase, *Ber.*, **91**, 1801 (1958).

[18] The ability of metal ions to mediate the dimerization of free radicals has been clearly demonstrated: J. K. Kochi and F. F. Rust, *J. Am. Chem. Soc.*, **83**, 2017 (1961).

If an ion like that depicted in (12) were initially formed in aqueous dimethylformamide, then surely it would rapidly lose a halogen atom to Cr^{++} (13) to result in an an ion (RCr^{++}) analogous to the ions described by Anet[9,6b] and noted above. Although not a strictly analogous comparison, it is noteworthy that the rate of reduction of $(H_2O)_5CrCl^{++}$ by Cr^{++} in water is indeed quite rapid; H. Taube and E. L. King, *J. Am. Chem. Soc.*, **76**, 4053 (1954). Thus an alternate path for the dimerization might be (12) followed by eq. 13 and 14.

$$RCrX^{++} + Cr^{++} \longrightarrow CrX^{++} + RCr^{++} \qquad (13)$$
$$RCr^{++} + RCl \longrightarrow R_2 + CrCl^{++} \qquad (14)$$

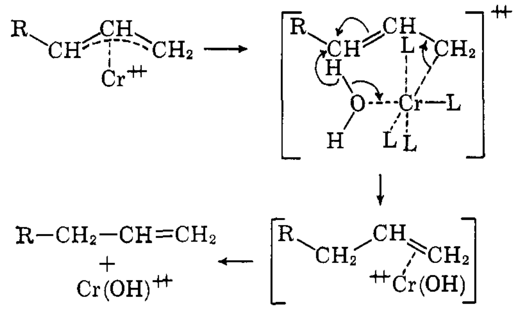
However, the high proportion of *meso*-2,3-diphenylbutane obtained from the coupling of the α-phenylethyl halides mitigates against (14).

[19] Both the forward[9] and the reverse[18] processes depicted in (15) have been noted and in light of these observations it is reasonable that (15) should be operative in these reactions. Furthermore, relatively high concentrations of Cr^{++} would decrease the steady-state concentration of free radicals to the point where the dimerization of these entities, or their attack upon RCr^{++}, becomes negligible. In this circumstance the ion RCr^{++} may dissociate in an irreversible heterolytic fashion to yield alkane.

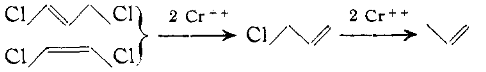
[20] Alternatively, path 13, footnote 18, would accommodate the stereochemistry of the reductions of the allylic butenyl chlorides if the intermediate ions should be depicted as π-allyl complexes of chromium; *cf.*, W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

[21] Stoichiometric ratios of 2 Cr^{++} to 1 allyl chloride yield only propylene; however, whether or not dimerization will occur at lower ratios of initial concentration of reactants for this and other substrates bears further investigation.

[22] J. G. Aston, *et al.*, *J. Chem. Phys.*, **14**, 77 (1946).


(18)

olefin allyl chloride (19), for none of the vinyllic chloropropenes are reduced by Cr^{++}. These results are entirely in accord with the path sketched in (18). That is to say, the nature of the olefinic product obtained in the reduction of allylic halides by Cr^{++} is controlled by the stability of an intermediate olefin Cr^{+3} complex. It will be noted that the stabilities of related transition metal–olefin complexes[23] are in the order terminal olefin >> *cis*-olefin > *trans*-olefin.


(19)

Recent studies of the oxidation of free radicals by Cu^{++} [24] and, in particular, the thorough study of the copper salt-catalyzed reaction of butenes with peresters by Kochi[24c] have pointed up the very high yields of terminal olefins in a reaction that entails the oxidation of a free radical by Cu^{++}. The process has been described to occur within a Cu^{++} complex. It would seem then that coordination and group or proton transfer within a metal ion complex may be important features of both the oxidation of free radicals by Cu^{++} and the complimentary process, their reduction by Cr^{++}.

Experimental

All operations involving Cr^{++} were carried out in a nitrogen atmosphere.

Materials.—Chromous sulfate solutions were prepared by the zinc powder reduction of $Cr_2(SO_4)_3 \cdot XH_2O$ in the manner previously described.[1] Transfers and storage of this solution, and analyses for Cr^{++}, were handled in like fashion. The clear blue solutions employed in this work were usually ~0.5 *M*. The Cr^{++} titer remained constant for months.

Solid chromous sulfate pentahydrate was prepared for use in the kinetic runs according to the procedure of Lux and Illman.[25] In our hands the large blue crystals were not quite as stable in air as indicated by these authors, but they were easily stored without decomposition under N_2. The best looking crystals were obtained by washing the crude substance with ice–water under N_2 and removing the excess water *in vacuo* at room temperature under N_2.

The physical properties of the following substances checked those of the literature and they were employed without purification: Eastman Kodak White Label methylene bromide and α-phenylethyl bromide, Matheson Coleman and Bell *n*-propyl bromide, isopropyl bromide, *t*-butyl bromide, *p*-bromophenacyl bromide, phenacyl chloride, and β-phenylethyl bromide. The following were freshly distilled before use and their physical constants were those of the literature: allyl chloride, allyl bromide, allyl iodide, α-phenylethyl chloride, 1,4-dibromobutane, and dimethylformamide. The *cis*- and *trans*-1,3-dichloropropenes were obtained by careful repeated fractionation of commercial Telone through a center rod column. The pure *cis* isomer had b.p. 103° (745 mm.). Gas chromatographic analysis (10 ft. × 0.25 in. DC-710 column) showed the halide to be uncontaminated with the *trans* isomer. A fraction of the *trans* isomer having a low b.p. 106–107.5° and containing 94% *trans*, 6% *cis* (v.p.c.) was further purified gas chromatographically. A 10 ft. × $^3/_8$ in. 20% DC-710 column was used for trapping. The collected material was 99.6% *trans*-, 0.4% *cis*-1,3-dichloropropene. The crotyl halides were prepared from the respective carbinols[12a,b] and repeatedly fractionated. The *cis* isomer had b.p. 83–83.5°, n^{22}D 1.4393, and the *trans*, b.p. 83.5°, n^{23}D 1.4331. The isomeric 3-chlorobutene-1 was prepared according to Kharasch[26]; b.p. 62.4°, n^{21}D 1.4150. The purity of the crotyl halides was assayed by their reduction with $LiAlH_4$ in tetrahydrofuran. The results are presented in Table III.

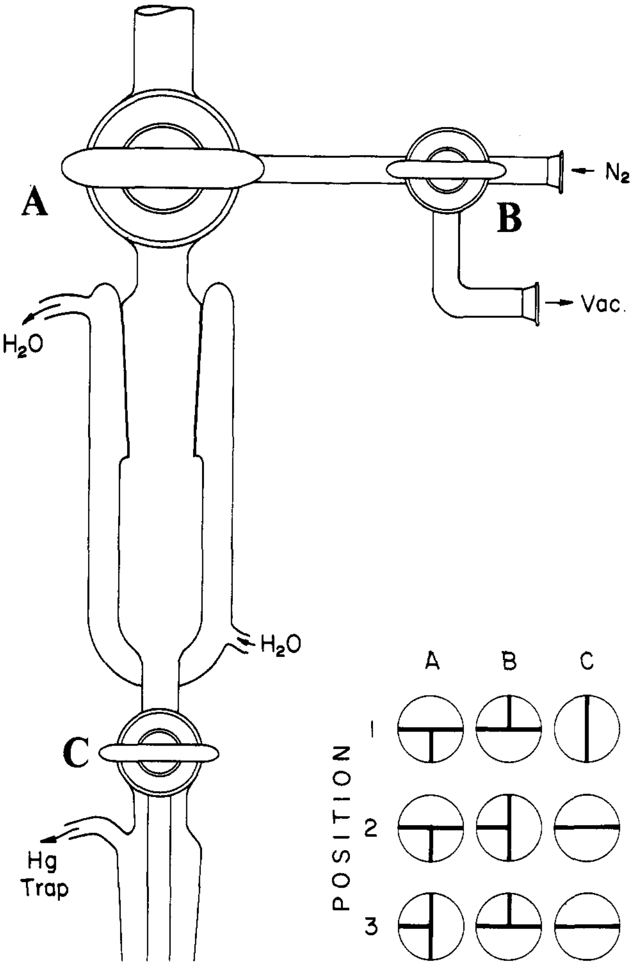


Figure 1.

Kinetic Runs.—The reactor (Fig. 1) employed in the kinetic runs was designed for the rapid removal and quenching of aliquots under nitrogen. It consisted of a 1-l. 3-neck flask fitted with a water-jacketed dropping funnel, stirrer, and nitrogen inlet and outlet. The outlet was connected to a Hg trap. The flask was immersed in a thermostat. A male 24/40 joint fused to the bottom of the flask protruded through the bottom of the water bath and connected to the sampling assembly sketched in the accompanying figure. All stopcocks were wide bore. The stirrer was fitted with an extra blade to agitate adequately the solutions just above the sampling assembly. Thermostat water was rapidly circulated about the water-jacketed addition funnel and sample cavity. In general, solid $CrSO_4 \cdot 5H_2O$ was dissolved in H_2O in the reaction flask and an equal volume of dimethylformamide was added. The dropping funnel was charged with a solution of the halide in 50% aqueous dimethylformamide. The sample cavity had a volume of 46.5 ml. The quenching solution, 50 ml. of 0.1 *M* $FeCl_3$, was placed in a 250-ml. erlenmeyer flask and fitted to the bottom joint of the sampling assembly. Before commencing a run, an aliquot of the prepared $CrSO_4$ solution was removed for analysis. With the stopcocks in position 1, the sample cavity and quench solution were thoroughly flushed with N_2. The sample cavity was next evacuated (position 2), filled (position 3), and quenched (position 4). Although it was not necessary in the present work, aliquots could handily be removed at 30-sec. intervals in this fashion. The quenched solutions after dilution were titrated to the green ferric phenantholine end point with 0.1 *M* $Ce(SO_4)_2$.

For smaller scale, relatively slow runs, a reaction flask like that described for the reductions was used. Samples were withdrawn with a hypodermic syringe.

The Cr^{++} Reductions.—The reduction of allyl bromide by chromous sulfate is presented as a typical case. Other substrates were allowed to react in similar fashion.

The Reduction of Allyl Bromide.—A calibrated, nitrogen-preflushed glass syringe fitted with a hypodermic needle was used to

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transfer 100 ml. of 0.301 *M* $CrSO_4$ (0.0301 mole) into the reaction flask of a calibrated apparatus that was equipped with: N_2 inlet and outlet, vacuum, a serum cap fitted to a stopcock, a manometer, magnetic stirring bar, and addition funnel. The addition funnel was charged with a solution of 1.213 g. of allyl bromide (0.010 mole) dissolved in 100 ml. of dimethylformamide (DMF). The system, under nitrogen, was evacuated to 60 mm. With rapid stirring, the halide solution was added all at once. Upon contact the blue solution became green and vigorous gas evolution commenced. When the gas evolution had ceased (*ca.* 30 min.), the pressure change corresponded to 0.0101 mole[27] of gas. The system was filled with N_2. The withdrawal of duplicate 5-ml. aliquots of the reaction solution indicated, upon titration, that 0.0206 mole of Cr^{++} had been consumed. The gas was identified as propylene by its characteristic emergence time on a 30-ft. dimethylsulfolane gas chromatographic column at room temperature, and by its infrared spectrum which was identical with authentic propylene.

Allyl chloride (0.769 g., 0.010 mole) in 100 ml. of DMF was treated with 100 ml. of 0.301 *M* $CrSO_4$ (0.0301 mole). After 1.5 hr., 0.0148 mole of Cr^{++} was consumed and 0.0072 mole of propylene was produced.

Allyl iodide under the same conditions reacted rapidly to produce propylene. The stoichiometry was not ascertained.

n-**Propyl bromide** (1.293 g., 0.0105 mole) in 100 ml. of DMF was treated with 100 ml. of 0.518 *M* $CrSO_4$. The reaction mixture slowly turned green. After 3 days, 0.00506 mole of Cr^{++} had been consumed and 0.00264 mole of propane had been produced.

Isopropyl Bromide.—After 3 days isopropyl bromide (0.0101 mole) consumed 0.00636 mole of Cr^{++} and 0.00315 mole of propane was obtained.

t-**Butyl bromide** (1.370 g., 0.0100 mole) in 100 ml. of DMF was allowed to react with 100 ml. of 0.363 *M* $CrSO_4$. Vigorous gas evolution ensued. Chromous was consumed rapidly at first, but after 1 hr., only 0.0015 mole of Cr^{++} had reacted. The gas was found to be 12.7% isobutane and 87.3% isobutylene. The same experiment was repeated substituting Cr^{+3} for Cr^{++} and isobutylene was again rapidly produced. The isobutylene is not a product resulting from interaction of the halide with Cr^{++}. Apparently tertiary halides rapidly dehydrohalogenate in this media. Isobutylene is not reduced by Cr^{++}.

Methylene Bromide.—Dibromomethane (1.189 g., 0.00683 mole) in 50 ml. of DMF was treated with 100 ml. of 0.5181 *M* Cr^{++}. Reaction was instantaneous. After 10 min., 0.0261 mole of Cr^{++} had been consumed and 0.0066 mole of methane produced.

Ethylene dibromide (2.10 g., 0.0111 mole) dissolved in 50 ml. of DMF was allowed to react with 50 ml. of 0.446 *M* $CrSO_4$ (0.0223 mole). The reduction was extremely rapid. After 1 hr., 0.0184 mole of Cr^{++} was consumed and 0.0092 mole of ethylene was obtained.

1,4-Dibromobutane (0.797 g., 0.00371 mole) dissolved in 50 ml. of DMF was treated with 51.05 ml. of 0.471 *M* $CrSO_4$ (0.0241 mole). After 5 days, 0.0117 mole of Cr^{++} was consumed. *n*-Butane was the only gas evolved. In another identical run, after 1.7 days, 0.0061 mole of Cr^{++} was consumed and only 0.00765 mole of *n*-butane was produced. The reaction which must proceed by way of *n*-butyl bromide was not quantitized. Analysis for *n*-butyl bromide was not attempted.

cis-**1,3-Dichloropropene.**—The halide (0.380 g., 0.00346 mole) in 50 ml. of DMF was allowed to react with 51.05 ml. of 0.471 *M* $CrSO_4$ (0.0241 mole). The reaction was 88% complete after 30 min. After 1.5 hr., 0.0127 mole of Cr^{++} had been consumed and 0.00324 mole of propylene produced. The reaction solution was steam distilled and ether extracted in order to isolate traces of the chloropropenes. None could be detected in either the steam distillate or in the DMF–metal ion solution after dilution and extraction.

trans-**1,3-Dichloropropene** (0.400 g., 0.00363 mole) in 50 ml. of DMF was allowed to react with 51.05 ml. of 0.471 *M* $CrSO_4$ (0.0241 mole). After 2.6 hr., 0.0133 mole of Cr^{++} had been consumed and 0.00343 mole of propylene was produced.

3-Chlorobutene-1 (0.334 g., 0.00368 mole) in 50 ml. of DMF was treated with 51.05 ml. of 0.471 *M* $CrSO_4$ (0.0241 mole). After 1.5 hr., 0.0059 mole of Cr^{++} had reacted and 0.00311 mole of butenes was produced. The composition of the butenes was determined by gas chromatography with a 30-ft. × 0.25 in. dimethylsulfolane column at room temperature. The butenes were cleanly resolved on this column.

cis-**Crotyl chloride** (0.305 g., 0.00337 mole) in 50 ml. of DMF was treated with 51.05 ml. of 0.471 *M* $CrSO_4$ (0.0241 mole). After 40 min. 0.0056 mole of Cr^{++} had reacted and 0.00288 mole of butenes were produced.

trans-**Crotyl Chloride.**—Under identical conditions, 0.312 g. (0.00344 mole) of the *trans*-halide, after 1.5 hr., had consumed 0.0057 mole of Cr^{++} and produced 0.00271 mole of butenes.

A mixture of 71% *trans*- and 29% *cis*-crotyl chloride (0.331 g., 0.0366 mole) under the same conditions, after 1.5 hr., had consumed 0.0061 mole of Cr^{++} and produced 0.00318 mole of butenes.

The $LiAlH_4$ Reduction of the Butenyl Chlorides.—In a typical run, 1.0 g. of halide in 5 ml. of tetrahydrofuran was treated with 0.8 g. of $LiAlH_4$ suspended in 10 ml. of tetrahydrofuran at room temperature. After 15 min., gas samples were withdrawn for the v.p.c. analysis.

p-**Bromophenacyl Bromide.**—In a 3-neck flask equipped with a dropping funnel, stirrer, nitrogen inlet and outlet (connected to a Hg trap), and a stopcock fitted with a serum cap, was placed 50 ml. of 0.317 *M* $CrSO_4$ (0.0159 mole) under N_2. The dropping funnel was charged with 2.30 g. (0.0079 mole) of *p*-bromophenacyl bromide in 100 ml. of DMF. The solutions were mixed and reaction took place immediately. After several minutes, crystals appeared floating in the reaction mixture. The reaction was allowed to proceed overnight at room temperature. Analysis for Cr^{+2} showed that 0.015 mole had been consumed. The white crystals floating on top of the reaction mixture were filtered off, washed with water, and dried; 0.074 g. of di-(*p*-bromobenzoyl)-ethane (0.000187 mole) was obtained, m.p. 175°. The substance was recrystallized from benzene; m.p. 182° (lit. 182°). *Anal.* Calcd. for $C_{16}H_{12}O_2Br_2$: C, 48.48; H, 3.03. Found: C, 48.17; H, 2.90. The infrared spectrum of the substance corroborated this structure.

The reaction mixture was then fractionally steam distilled. The steam distillate and the residue were extracted with chloroform. The combined extracts provided 1.44 g. of *p*-bromoacetophenone (0.0072 mole) which melted at 50°. The crystals were purified by steam distillation; m.p. 51° (lit. 51°); 2,4-dinitrophenylhydrazone, m.p. 237° (lit. 237°). The infrared spectrum of the sample was identical with that of a known sample.

Phenacyl Chloride.—Under the same conditions described for the reduction of *p*-bromophenacyl bromide, 1.24 g. of phenacyl chloride (0.00805 mole) was dissolved in 100 ml. of DMF and allowed to react with 50 ml. of 0.368 *M* Cr^{+2} (0.0184 mole). The reaction took place rapidly; however, it was allowed to proceed overnight at room temperature; 0.0129 mole of Cr^{+2} was consumed. The reaction mixture was steam distilled and the steam distillate was extracted with ether. The ether extract was dried over anhydrous $CaCl_2$ and the ether removed, providing 0.7643 g. of acetophenone (0.00637 mole), $n^{21}D$ 1.5327 (lit. $n^{20}D$ 1.5341), 2,4-dinitrophenylhydrazone m.p. 249° (lit. 250°). The infrared spectrum of the sample was identical with that of a known sample.

β-**Phenylethyl Bromide.**—In similar fashion, 1.540 g. of *β*-phenylethyl bromide (0.00830 mole) was dissolved in 100 ml. of DMF and treated with 100 ml. of 0.363 *M* $CrSO_4$ (0.0363 mole). The reaction proceeded slowly and was allowed to continue for 2 days. Analysis for Cr^{+2} showed that 0.00370 mole had been consumed. The reaction mixture was then distilled into 50 ml. of carbon tetrachloride until DMF began coming over. The carbon tetrachloride solution was then washed with water to remove any DMF and dried over anhydrous Na_2SO_4. Qualitative and quantitative gas chromatographic analysis of the carbon tetrachloride solution was effected on a 6-ft. Dow Corning 710 column. In this way 0.00178 mole of ethylbenzene was detected. The ethylbenzene peak was trapped and its infrared spectrum was found to be identical with that of a known sample.

α-**Phenylethyl Bromide.**—*α*-Phenylethyl bromide (5.548 g., 0.030 mole) was dissolved in 100 ml. of DMF and treated with 100 ml. of 0.460 *M* $CrSO_4$ (0.0460 mole). The reaction began immediately and after several minutes crystals appeared floating in the reaction mixture. The reaction was allowed to proceed overnight at room temperature. Analysis for Cr^{+2} showed that 0.0186 mole had been consumed. The reaction mixture was filtered and the white crystals were washed with water and dried. In this way 1.77 g. of *meso*-2,3-diphenylbutane was isolated, m.p. 123–125°. The compound was recrystallized from ethanol, m.p. 126–127° (lit. 126–127°). *Anal.* Calcd. for $C_{16}H_{18}$: C, 91.53; H, 8.57. Found: C, 91.69; H, 8.97.

The reaction mixture was then extracted four times with 150-ml. portions of ether. The ether extract was concentrated to 50 ml., washed with water to remove any DMF, and dried over anhydrous Na_2SO_4. Evaporation of the ether afforded 0.05 g. of *dl*-2,3-diphenylbutane, $n^{22}D$ 1.5540 (lit. $n^{20}D$ 1.5552). The total yield of 2,3-diphenylbutane was 0.0087 mole.

α-**Phenylethyl Chloride.**—The same procedure described for the reduction of *α*-phenylethyl bromide was used; 3.5126 g. of *α*-phenylethyl chloride (0.0250 mole) was treated with 0.0353 mole of Cr^{+2}; 0.0245 mole of Cr^{+2} was consumed and 2.49 g. of 2,3-diphenylbutane (0.0119 mole) was obtained. The isomer distribution was 85% *meso* and 15% *dl*. The products were identified by comparison with those obtained from the reduction of *α*-phenylethyl bromide.

Scanning was conducted in the following manner: A small amount (~0.05 g.) of the substrate was dissolved in 5 ml. of DMF and placed in a 25-ml. flask fitted with a serum cap. The flask was flushed with nitrogen and 5 ml. of $CrSO_4$ solution was added. A positive pressure of nitrogen was left in the flask and

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(27) In this and other runs the final pressure was in the range 100–300 mm. The solubility of the hydrocarbon gases under those conditions was not appreciable.

it was allowed to stand for 48 hr. at room temperature. A blank was also prepared. A color change from blue to green indicated that reaction had taken place. An additional check was provided by analysis for Cr^{++} and comparison with the blank.

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[CONTRIBUTION FROM THE JAMES BRYANT CONANT LABORATORY OF HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

The Rate of Mercuration of Benzene as a Function of the Activity of Water

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Earlier research had shown that neutral salts strongly accelerate the mercuration of benzene in dilute aqueous acid; the present work shows that 7.5 *M* sodium perchlorate increases the rate 300-fold. The reaction is not acid-catalyzed; the acceleration is not an effect of the salts on the acidity functions H_0 or H_R but rather is caused by the progressive removal of water from the mercuric ion. This conclusion is based upon the correlation between the rate of mercuration and the vapor pressure of water above the solutions; the second-order rate constant is an inverse monotonic function of $\mathbf{a}_{H_2O}$. A function Hg_0 describes the activation of Hg^{++} as water is withdrawn from it, much as H_0 describes the activation of H^+ under like conditions. The primary deuterium isotope effect is large, so the mechanism of mercuration involves rate-limiting deprotonation of $C_6H_5HHg^{++}$. The kinetics are complicated by extensive polymercuration; σ^+ for the Hg(II) substituent is only about 0.1. The relative rates of mono-, di-, and trimercuration were estimated from product analyses, and the system of kinetic equations was solved with the aid of an analog computer.

Introduction

The mercuration of benzene with mercuric perchlorate in aqueous solution is strongly accelerated by the addition of perchloric acid or of its neutral salts[2-4]; the present work shows that 7.5 *M* sodium perchlorate increases the rate in the presence of 0.5 *M* perchloric acid by a factor of 300. The rates are large compared to those for mercuration with the complexes of mercuric ion, such as the acetate. The acceleration by salts had previously[3] been ascribed to the formation of a reactive mercuric perchlorate complex, or alternatively[5] to a partially dehydrated mercuric ion which might be formed in the solution as the ions of the neutral salt, because of their own hydration, reduced the availability of water. But prior to the present work, the mode of action of salts was suspect. All the mercuration reactions are necessarily conducted in the presence of a small amount of mineral acid, since otherwise mercuric ion undergoes hydrolysis to form $Hg(OH)^+$, or to precipitate the oxide from solution. Further, neutral salts have a pronounced effect upon the acidity functions[6,7] of the solvent; our own work shows that 7.3 *M* $NaClO_4$ makes the H_0 value of 0.5 *M* $HClO_4$ 1.8 units more negative, and 6.3 *M* $NaClO_4$ makes the H_R value of 1.57 *M* $HClO_4$ 2.8 units more negative. Therefore the effect of neutral salts might have proved to be only that of lowering H_0 (or some alternative acidity function), mercuration would then be acid-catalyzed. This idea has proved incorrect; our findings show that the rate of mercuration is not affected by acidity *per se*, but is an inverse function of the activity of water in the solution.

The kinetics of the mercuration of benzene was followed by titration of the reaction mixture with thiocyanate; Hg^{++} requires two equivalents, whereas arylmercuric ions require but one for each equivalent of bound mercury(II). The reactions were generally carried out in the presence of a large excess of benzene, so that the aqueous solutions remained saturated. Thus in any experiment, the concentration of benzene was constant, whereas that of the phenylmercuric ion increased with time. Under our experimental conditions, phenylmercuric ion is further mercurated; the positively charged mercuric ion does not deactivate the ring strongly.

$$C_6H_6 + Hg^{++} \xrightarrow{k} C_6H_5Hg^+ + H^+$$

$$C_6H_5Hg^+ + Hg^{++} \xrightarrow{\alpha k} C_6H_4Hg_2^{++} + H^+$$

$$C_6H_4Hg_2^{++} + Hg^{++} \xrightarrow{\beta k} C_6H_3Hg_3^{+++} + H^+$$

The composition of the mixed product was obtained by converting the mercurated benzenes to bromobenzenes; *e.g.*

$$C_6H_5HgCl + Br_2 \longrightarrow C_6H_5Br + HgBrCl$$

The bromobenzenes were then analyzed by vapor-phase chromatography and infrared spectroscopy.

The chemical equations above lead to a complicated set of differential equations, which were handled with the aid of an analog computer. The solubilities of benzene were determined for enough solutions to allow an estimate of the concentration under each set of experimental conditions. The H_0 and H_R values of the solutions and their vapor pressures were measured, and the rates of mercuration compared with each of these functions.

Experimental

Materials.—Fisher Certified ACS benzene (thiophene-free[8]) was used without further purification. Benzene-d_6 was obtained from Merck of Canada, Ltd. Reagent grade perchloric acid (B & A, J. T. Baker, and Merck) was standardized against Merck Reagent sodium borate. Fischer purified sodium perchlorate monohydrate was recrystallized from water and dried to the anhydrous salt *in vacuo* at 95°; it contained less than 0.01% chloride. Anhydrous lithium perchlorate (Foote Mineral Co.) was twice recrystallized from water and vacuum dried, first at 95° and then at 140°. Solutions of mercuric perchlorate were prepared by dissolving yellow mercuric oxide (Mallinckrodt A.R.) in excess perchloric acid (with or without added salt) and filtering through a sintered glass funnel. Standard solutions of mercuric nitrate were prepared from triple-distilled mercury and nitric acid. Standard solutions of potassium thiocyanate were made up by weight from dried Mallinckrodt A.R. material. Bromobenzene, *o*-, *m*-, and *p*-dibromobenzene, and *sym*-tribromobenzene were Eastman White Label products, purified when required. 1,2,4-Tribromobenzene was prepared by the bromination of *p*-dibromobenzene in the presence of ferric and aluminum chlorides; the final product (m.p. 37–38°, lit. value[9] 43°) was better than 99% pure, as estimated by vapor-phase

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