In those cases where cupric acetate was employed in the photolytic decarboxylations, a $\mathrm{Cu^{II}}$–$\mathrm{Pb^{IV}}$ solution was prepared in an amber erlenmeyer flask. Aliquots of the homogeneous solution were then pipetted into the quartz tubes and the above procedure followed. The progress of these reactions could be followed by a color change from green to the blue of cupric acetate.

Analytical Procedures. The $\mathrm{Pb^{IV}}$ content of the starting lead tetraacetate and the unconsumed $\mathrm{Pb^{IV}}$ in the reaction mixtures were determined by iodometric titration according to the procedure of Kharasch and Friedlander.[32] Known components in the crude reaction mixtures were shown not to interfere with the analysis.

Reaction mixtures were analyzed by quantitative gas chromatography (glpc) using various internal standards which were previously calibrated against the individual reaction products. Identification of gas chromatographic peaks was verified by comparing their gas chromatography retention times with authentic compounds on at least two columns with different separation properties, *e.g.*, boiling point column and polar column. Moreover, identification was confirmed by chemical degradation of the reaction products. Typical cases are cited below.

Gas chromatographic analyses of gaseous and lower boiling hydrocarbons were performed on Case-constructed instruments, equipped with thermal conductivity detectors. Other analyses were performed on instruments with hydrogen flame ionization detectors: Aerograph, Model 200, dual column chromatograph, and Aerograph HiFy, Model 600-D.

Product Analysis from α,α-Dimethylphenylacetic Acid. Three principal products, α-methylstyrene, α-cumyl alcohol, and α-cumyl acetate, were identified by retention times which corresponded with those of authentic materials. Glpc analysis of the worked up reaction mixture after mild basic hydrolysis (0.5 *M* alcoholic KOH) revealed the absence of the ester component and a corresponding increase in the cumyl alcohol peak. Glpc analysis of the original reaction mixture or that resulting from basic hydrolysis yielded only one large peak corresponding to α-methylstyrene after treatment with dilute perchloric acid. While basic hydrolysis only saponified the ester, treatment with dilute mineral acid also caused dehydration. Hydrogenation of the original worked-up reaction mixture or the hydrolyzed mixtures moved the peak corresponding to α-methylstyrene to a new retention time corresponding to that of authentic cumene.

Acknowledgment. We wish to thank the Air Force Office of Scientific Research for a generous grant to support this research.

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[32] M. Kharasch, H. Friedlander, and W. Urry, *J. Org. Chem.*, **16**, 533 (1951).

The Mechanism of Reductive Elimination of *vic*-Dihalides by Chromium(II)

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Abstract: Reductive elimination of *vic*-dihalides and their analogs to alkenes by $\mathrm{Cr^{II}}$ is similar to reduction of alkyl halides and peroxides to alkanes. Kinetic studies show the mechanism of both involve multistep sequences. Stereochemical studies on *cis*- and *trans*-1,2-dibromocyclohexanes support Kray and Castro's hypothesis that a β-bromine has a neighboring group effect in the removal of the first halogen by ligand transfer to $\mathrm{Cr^{II}}$. The resulting β-haloalkyl radicals yield alkenes in reductive eliminations by three competing processes. At low $\mathrm{Cr^{II}}$ concentrations, the β-bromoalkyl radical fragments to bromine atom and alkene, whereas at higher concentrations a β-bromoalkylchromium intermediate is postulated. *cis* elimination of $\mathrm{Cr^{III}Br}$ or *trans* elimination of bromide and $\mathrm{Cr^{III}}$ are competing routes of heterolysis of the bromoalkylchromium complex. These studies are also supported by the extremely facile reductive elimination of β-haloacyl peroxides by $\mathrm{Cr^{II}}$; $\mathrm{Cr^{III}}$ species and halide are quantitatively separated and identified by ion-exchange chromatography. A variety of other β-substituted alkyl halides also yields alkenes with $\mathrm{Cr^{II}}$. Kinetic studies show that chloro-, tosyloxy-, hydroxy-, and acetoxyalkyl bromides are reduced much slower than vicinal dibromides and a significantly smaller neighboring group assistance by β-chloro, β-tosyloxy, β-hydroxy, and β-acetoxy groups in the removal of the initial bromine by $\mathrm{Cr^{II}}$ is indicated. Furthermore, fragmentation of the free radical and *trans* elimination of the alkylchromium intermediate are less important processes with β-chloro-, -hydroxy, and -acetoxyalkyl moieties compared to the β-bromo analog. The former appear to undergo reductive elimination exclusively by a concerted *cis* departure of a complexed $\mathrm{Cr^{III}}$ species from the β-substituted alkylchromium intermediate. On the other hand, the facile removal of a β-toxyloxy group may proceed largely *via* a transoid transition state.

A variety of organic halides are reduced by chromous compounds, which are commonly accessible and versatile reducing agents.[1] The rates of reduction and products are dependent on the structure of the organic halide. Among those classes of halides readily reduced are α-aralkyl halides, allylic halides, and α-halocarbonyl and cyano compounds. The former generally requires 2 moles of $\mathrm{Cr^{II}}$[2] per mole of halide and affords products of bimolecular reduction (eq 1)[3] whereas the latter two types of halides undergo simple reduction (eq 2).[1]

$$\mathrm{2RX + 2Cr^{II} \longrightarrow R_2 + 2[Cr^{III},X^-]} \qquad (1)$$

$$\mathrm{RX + 2Cr^{II}(SH) \longrightarrow RH + 2Cr^{III}(X^-,S^-)} \qquad (2)$$

Alkyl and vinyl halides are practically unreactive to $\mathrm{Cr^{II}}$ and require prolonged exposure in order to effect even partial reduction. On the other hand, if $\mathrm{Cr^{II}}$ is complexed with ethylenediamine, the resulting species

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[1] For summaries, see (a) C. Castro and W. Kray, Jr., *J. Am. Chem. Soc.*, **85**, 2768 (1963); (b) L. Slaugh and J. Raley, *Tetrahedron*, 20, 1005 (1964); (c) J. Kochi and D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964).

[2] Unless specifically noted, chromous species are indicated as $\mathrm{Cr^{II}}$ without regard to the nature of solvation. Octahedrally coordinated chromous ion in these solvents is highly labile to substitution.

[3] J. Kochi and D. Buchanan, *J. Am. Chem. Soc.*, **87**, 853 (1965).

is a potent reducing reagent which affords alkanes,

$$RX + 2Cr^{II}en(SH) \longrightarrow R\text{-}H + 2Cr^{III}en(X^-,S^-) \qquad (3)$$

alkenes, and arenes from alkyl, vinyl, and aryl halides, respectively.[4,5]

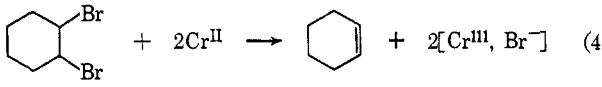
Unlike alkyl halides, geminal, vicinal, and 1,3-dihalides can be reduced by Cr^{II} to generate carbenes,[6] alkenes,[7] and cyclopropanes[8] by α-, β-, or γ-reductive elimination of both halogen atoms. The enhanced reactivity of vicinal dihalides compared to alkyl monohalides of analogous structure was first noted by Kray and Castro.[7b] For example, the relative rates of reduction of α-phenethyl chloride and styrene dichloride is 1:20. Replacement of the primary chlorine by bromine increases the rate of the latter by a factor of 2.5. They attributed the activating influence of a β-halogen atom, particularly bromine, to its neighboring group effect in assisting removal of the first halogen by Cr^{II}.

The rates of reduction of organic halides by Cr^{II} or Cr^{II}en increase in the order Cl < Br < I. For benzyl halides, the relative rates of reduction of iodide, bromide, and chloride by Cr^{II} in ethanol are 555, 124, and 1, respectively.[1c] Similarly, the reduction of *n*-butyl iodide, bromide, and chloride by Cr^{II}en in dimethylformamide solutions are in the order 5×10^3, 5×10^2, and 1, respectively.[9] A similar order of reactivity pertains to reduction of vicinal dihalides. Thus, ethylene dibromide is readily reduced by Cr^{II} under conditions in which ethylene chloride is unreactive.[7b]

Further examination of reductive elimination of *vic*-dihalides by Cr^{II} was undertaken in order to determine quantitatively the role of Cr^{II} in the removal of the first as well as the second halogen atom and to delineate the stereochemical requirements of the reaction. We also hope to compare and relate these reactions of *vic*-dihalides which produce alkenes with similar reductions of alkyl halides to alkanes by chromous reagent as a part of our interest in the mechanism of reduction of organic compounds by metal complexes.[10]

Results

Reductive Elimination of *vic*-Dibromocyclohexanes. Chromous perchlorate solutions in aqueous ethanol or dimethylformamide (DMF) were employed in reductive elimination of 1,2-dibromocyclohexanes. Perchloric acid and lithium perchlorate were added to maintain constant acidity and ionic strength of the medium. From both *cis*- and *trans*-1,2-dibromocyclohexanes, reduction with Cr^{II} in these media afforded cyclohexene in greater than 99% yield according to the stoichiometry given by eq 4.[11] A small but discrete (<0.5%) amount of bromocyclohexane was also produced. The reaction followed simple second-order kinetics, being first order each in Cr^{II} and dibromide to greater than 70% reaction. The second-order rate constant was independent of the initial Cr^{II} and dibromide over a wide range of concentrations, in accord with earlier studies on other systems by Kray and Castro.[7b]



(4)

In DMF solutions, the rate was accelerated slightly by increasing acid concentration and ionic strength as shown in Table I. The rate, however, was depressed by halide ion, added as the lithium salt. The molar depression in the rate by bromide was larger than by chloride, but was difficult to study due to analytical problems encountered with large amounts of bromide salts.

Table I. The Effects of Acidity and Ionic Strength on Reduction of Dibromocyclohexanes by Cr^{II} at 20° [a]

Cyclohexane	Solvent	H^+, *M*	[I],[d] *M*	$k \times 10^3$, l. mole^{-1} sec^{-1}
trans-1,2-Dibromocyclohexane	EtOH[b]	1.0	1.0	3.87 ± 0.15
	EtOH	0.2	1.0	4.85 ± 0.02
	EtOH	0.0	1.0	5.00 ± 0.14
	EtOH	0.0	0.0	4.95 ± 0.01
	DMF[c]	1.0	1.0	389 ± 19
	DMF	0.0	1.0	279 ± 11
	DMF	0.2	0.2	193 ± 10
	DMF	0.0	0.0	124 ± 6
cis-1,2-Dibromocyclohexane	DMF[c]	1.0	1.0	2.60 ± 0.15
	DMF	0.2	1.0	2.13 ± 0.07
	DMF	0.0	1.0	1.99 ± 0.05
	DMF	0.0	0.0	0.937 ± 0.043
Bromocyclohexane	DMF[c]	1.0	1.0	0.128
	DMF	0.2	1.0	0.128 ± 0.02
	DMF	0.0	1.0	0.0930 ± 0.0057
	DMF	0.0	0.0	0.0215

[a] Under these conditions the ratio equivalents of Cr^{II}/equivalents of RBr_2 was varied from 0.54 to 2.23. These runs yielded rate constants within the quoted range. [b] EtOH was 80–88% in strength, the rest being water and $HClO_4$. [c] DMF was 85–99%, the rest being water, ethanol, and $HClO_4$. [d] [I] refers to the molarity of *added* $LiClO_5$.[4] Perchlorate arising from $Cr(ClO_4)_2$ amounted to ≤0.2 *M*, except for *trans*-DMF where it was ≤0.02 *M*.

The effect of halides on Cr^{II} in DMF or ethanol was apparent by visual changes in color of the blue solutions. Examination of the absorption spectrum of Cr^{II} showed that the band at 696 mμ underwent a bathochromic shift and concomitant intensification, which were dependent on the molar ratio of halide and Cr^{II}. As chloride was increased, the intensity passed through a maximum ($Cl^-/Cr^{II} \approx 5$), but no such maximum appeared in the corresponding studies with bromide shown in Figures 1 and 2.

Several apparent but no well-defined isosbestic points could be established owing to the broadness of the absorption bands. Therefore, we could not definitely attribute the spectral shift to a single halochromium(II) species.[12] It is more likely that a series of such complexes are in equilibrium[13] (eq 5).

$$Cr^{II} + nX^- \rightleftharpoons Cr^{II}X_n^{+2-n} \qquad n = 0, 1, 2, \ldots \qquad (5)$$

These spectral studies strongly suggest that the adverse effect of chloride ion is due to its ability to displace

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[4] J. Kochi and P. Mocadlo, *J. Am. Chem. Soc.*, **88**, 4094 (1966).

[5] D. Singleton, unpublished observations.

[6] C. Castro and W. Kray, Jr., *J. Am. Chem. Soc.*, **88**, 4447 (1966).

[7] (a) P. Julian, W. Cole, A. Magnani, and E. Meyer, *ibid.*, **67**, 1728 (1945); (b) W. Kray and C. Castro, *ibid.*, **86**, 4603 (1964).

[8] J. Kochi and P. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965); J. Kochi and D. Singleton, in press.

[9] J. Powers, unpublished studies.

[10] J. Kochi, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 27, 207 (1966).

[11] The nature of the Cr^{III} and Br^- species is discussed later (*vide infra*).

[12] R. L. Pecsok and J. J. Lingane, *J. Am. Chem. Soc.*, **72**, 189 (1950); D. Holah and J. Fackler, *Inorg. Chem.*, **5**, 479 (1966).

[13] W. Malik, K. Abubacker, and M. Ajmal, *Indian J. Chem.*, **2**, 345 (1964).

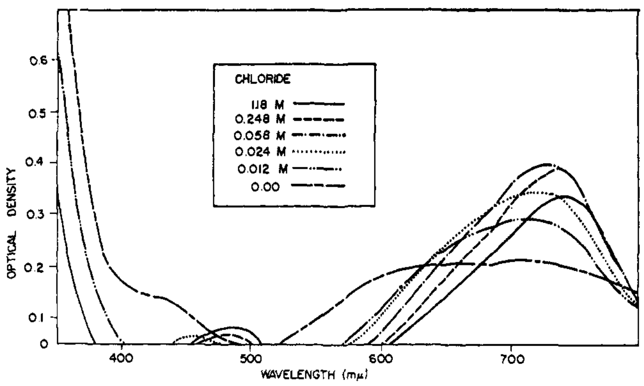


Figure 1. Absorption spectra of 0.0123 *M* Cr^{II} perchlorate in dimethylformamide in the presence of added lithium chloride.

DMF or ethanol from the coordination shell of Cr^{II}.[14] The kinetic effect is thus twofold in decreasing the concentration of Cr^{II} and yielding a less reactive chlorochromium(II) complex. Since the composition of the solvent used in kinetic studies varied somewhat, it was necessary to establish that such changes had a negligible effect on the rates. The rates of reductive elimination of *trans*-1,2-dibromocyclohexane in a number of solvent mixtures are listed in Table II. It is apparent that the rate in DMF depended both on the bulk composition of the solvent as well as the molar ratio of DMF/Cr^{II}. For solvents containing greater than 70% DMF an average second-order rate constant of $193 \pm 10 \times 10^{-3}$ l./mole sec was obtained and the rate was rather insensitive to composition in this region. Since most rate measurements were made in the range 85–99% DMF, the solvent composition was not a critical factor.

Table II. Reduction of Dibromocyclohexane by Cr^{II} in Ethanol–Water–DMF Solutions[a]

Solvent[b] (DMF), %	DMF/Cr^{II} ratio	$k \times 10^3$, l. mole^{-1} sec^{-1}
0.0	0.00	4.83
2.0	13.0	25.0
5.0	5.29	29.6
5.0	32.6	47.5
10.0	11.1	37.5
10.0	64.1	117
20.0	22.7	97.9
50.0	675	77.8[c]
60.0	810	162
70.0	943	189
80.0	1130	205
90.0	1230	179
95.0	1350	193
98.2	1380	199

[a] *trans*-1,2-Dibromocyclohexane in DMF–water and DMF–EtOH mixtures at 20°. Acidity held at 0.2 *M* $HClO_4$ with no additional perchlorate. [b] For DMF <50% v/v the system was DMF–EtOH (H_2O <12%). For DMF ≥50% v/v the system was DMF–water (EtOH <1%). [c] The rate plot was badly curved for this run. It was suspected that the mixture was inhomogeneous. Rate constant was estimated from initial rate.

The sharp increase in rate of reduction on proceeding from ethanol to dilute solutions of DMF can be attributed to a change in coordination around Cr^{II} from

$$Cr^{II}(EtOH)_6 + 6DMF \rightleftarrows Cr^{II}(DMF)_6 + 6EtOH \qquad (6)$$

ethanol to DMF (eq 6). The latter is a more reactive reducing agent than the former, but is not as effective as Cr^{II} complexed with ethylenediamine or ethanolamine.[4]

The reductive rates of *cis*- and *trans*-1,2-dibromocyclohexanes by Cr^{II} were examined over a range of temperatures given in Table III and compared to the slower reduction of bromocyclohexane to cyclohexane. Overlapping ranges of temperature had to be employed owing to wide variations in rates. The activation parameters for these reductions are given in Table IV.

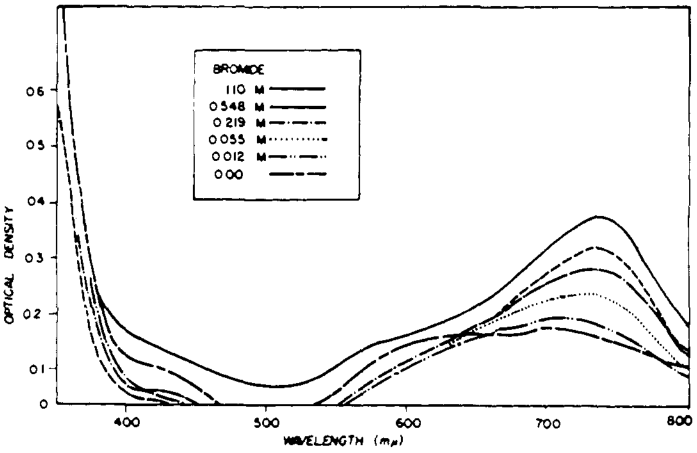


Figure 2. Absorption spectra of 0.0123 *M* Cr^{II} perchlorate in dimethylformamide with added lithium bromide.

Chromium(III) and Bromide Products from Reductive Elimination. The stoichiometry of reductions by Cr^{II}, especially with respect to the fate of chromium and bromine, provides considerable insight into the details of the mechanism. First, in order to examine these products the simple reduction of allyl bromide to propylene by Cr^{II} was chosen because of the rapid rate of reduction. Propylene was formed quantitatively in ethanol containing 0.9 *M* perchloric acid at 0° according to the stoichiometry given in eq 7.[7b] Ethanol and

$$CH_2{=}CHCH_2Br + 2Cr^{II}(EtOH, H_2O) \longrightarrow CH_3CH{=}CH_2 + Cr^{III}Br + Cr^{III} \qquad (7)$$

not DMF was chosen as solvent for these studies owing to difficulties encountered in the ion exchange of Cr^{III}-(DMF) species.[14] Ion exchange at 0° in Dowex 50W-X12 established that reduction with excess Cr^{II} (0.080 *M*) leads to 1 mole of $Cr^{III}Br$ per mole of allyl bromide. Aquation of $Cr^{III}Br$ which is catalyzed by Cr^{II} was a minor competing reaction (*vide infra*). Bromide ion so produced was determined by argentic titration and a small blank (1.5–3%) was subtracted to account for this solvolysis. In the presence of excess allyl bromide (0.091 *M*), a solution of 0.080 *M* Cr^{II} produced a 16–20% excess of $Cr^{III}Br$ relative to propylene in eq 7. Less than 0.3% biallyl was formed in the reaction under these conditions, so that the excess $Cr^{III}Br$ did not arise from a possible coupling of allyl

[14] The $Cr^{II}(DMF)_6$ complex can be readily demonstrated by examination by ion exchange of the $Cr^{III}(DMF)_6$ species formed on oxidation (*vide infra*). Aqueous solutions of Cr^{III} obtained from oxidation of Cr^{II} by alkyl halides in ethanol can be readily separated by ion exchange in Dowex 50W-X12. $Cr^{III}(DMF)_6$ species obtained from oxidation of Cr^{II} in DMF, on the other hand, are poorly separated and require a less highly cross-linked resin to achieve elution owing to their much larger ionic diameters; *cf.* Cr^{III} methanol complexes, R. Baltisberger and E. King, *J. Am. Chem. Soc.*, **86**, 795 (1964).

Table III. Temperature Dependence on Rate of Reduction of Dibromocyclohexanes[a]

Halide	Temp, °C	No. of runs	$k \times 10^3$,[b] l. mole^{-1} sec^{-1}
trans-1,2-Dibromocyclohexane	−0.60 ± 0.04	2	84.8 ± 2.1
	5.00 ± 0.04	2	137 ± 0
	10.00 ± 0.05	4	177 ± 12
	15.30 ± 0.06	2	295 ± 2
	20.00 ± 0.03	4	389 ± 12
cis-1,2-Dibromocyclohexane	10.00 ± 0.05	2	1.22 ± 0.04
	15.30 ± 0.06	2	2.05 ± 0.05
	20.00 ± 0.03	2	2.73 ± 0.03
	25.15 ± 0.05	2	4.14 ± 0.06
	29.74 ± 0.05	2	6.03 ± 0.20
Bromocyclohexane	29.75 ± 0.05	2	0.300 ± 0.026
	34.96 ± 0.05	2	0.474 ± 0.005
	39.75 ± 0.05	2	0.675 ± 0.001
	45.19 ± 0.05	2	0.875 ± 0.000
	49.70 ± 0.07	2	1.39 ± 0.08

[a] In 88% v/v DMF–water and 1.0 *M* perchloric acid. [b] Errors are observed limits of scatter.

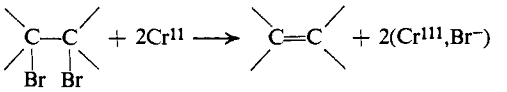
Table IV. Activation Parameters for Reduction of Dibromocyclohexanes by $\mathrm{Cr^{II}}$

Halide	Temp range, °C	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu
trans-1,2-Dibromocyclohexane	−0.6–20.0	11.2 ± 0.9[a]	−20.8 ± 2.5
cis-1,2-Dibromocyclohexane	10.0–29.7	13.2 ± 0.6	−24.2 ± 2.0
Bromocyclohexane	29.7–50.0	14.4 ± 1.3	−27.2 ± 4.5

[a] Errors are maximum errors computed by the method of R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Am. Chem. Soc.*, **83**, 3819 (1961).

bromide and allylchromium similar to that obtained with benzyl bromide.[3,15]

Reductive elimination of *vic*-dibromides also generates 2 moles of $\mathrm{Cr^{III}}$ products according to the stoichiometry given in eq 8. These consist of a mixture


(8)

of $\mathrm{Cr^{III}}$ and $\mathrm{Cr^{III}Br}$ which were separated and determined quantitatively by ion-exchange chromatography. Bromine was completely accounted for as free bromide and $\mathrm{Cr^{III}Br}$ and the sum of all the products containing bromine was equal to twice the yield of alkene.

$\mathrm{Cr^{III}Br}$ is a substitution-stable complex and liberation of bromide ion by aquation is rather slow. However, in the presence of excess $\mathrm{Cr^{II}}$ there was an induced reaction, which has been subsequently shown to be inversely dependent on the acid concentration.[16] The catalyzed solvolysis of $\mathrm{Cr^{III}Br}$, unlike other $\mathrm{Cr^{III}X}$–$\mathrm{Cr^{II}}$ exchanges, probably proceeds *via* a nonbridging ligand mechanism involving electron transfer.

$$\mathrm{{}^*Cr^{III}Br + Cr^{II} \longrightarrow {}^*Cr^{II}Br + Cr^{III}} \qquad (9)$$

$$\mathrm{{}^*Cr^{II}Br \overset{fast}{\rightleftharpoons} {}^*Cr^{II} + Br^-} \qquad (10)$$

In water the rate constant for hydrolysis decreases in the order[16] I (2×10^{-2} sec^{-1}) > Br (2×10^{-3} sec^{-1}) > Cl (4×10^{-4} sec^{-1}). In our systems the catalyzed solvolysis of $\mathrm{Cr^{III}Br}$ was only important when excess $\mathrm{Cr^{II}}$ was employed.

The relative amounts of bromide and $\mathrm{Cr^{III}Br}$ produced in the reductive elimination of *vic*-dibromides, expressed as $(\mathrm{X^-})/(\mathrm{Cr^{III}X} + \mathrm{X^-})$, varied according to the ratio of $\mathrm{Cr^{II}}$ and dibromide in the starting mixture. As shown in Table V, the amount of bromide ion *increased* with increasing $\mathrm{Cr^{II}}$ in the mixtures. The bromide ion formed by the $\mathrm{Cr^{II}}$-catalyzed solvolysis of $\mathrm{Cr^{III}Br}$ was corrected for by extrapolating the ratio $(\mathrm{Br^-})/(\mathrm{Cr^{III}Br} + \mathrm{Br^-})$ to zero time.

Table V. Halo $\mathrm{Cr^{III}}$ and Halide Formed in Reductive Eliminations with $\mathrm{Cr^{II}}$ [a]

Substrate, *M*		$\mathrm{Cr^{II}}$/substrate,[b] equiv/equiv	Halide[c]/(halide + $\mathrm{Cr^{III}Hal^{2+}}$)
trans-1,2-Dibromocyclohexane[d]	(0.11)	0.262	0.191 ± 0.016
	(0.027)	1.05	0.239 ± 0.009
	(0.014)	2.10	0.296 ± 0.036
	(0.0068)	4.20	0.331 ± 0.035
Styrene dibromide[d]			
	(0.11)	0.256	0.092 ± 0.003[e]
	(0.026)	1.08	0.106 ± 0.003
	(0.014)	2.06	0.142 ± 0.006
β-Bromopropionyl peroxide[f,g]	(0.37)	0.314	0.011 ± 0.002
	(0.092)	1.25	0.290
	(0.010)	2.77	0.299 ± 0.013
β-Chloropropionyl peroxide[f,h]	(0.11)	0.295	0.003 ± 0.001
	(0.011)	2.95	0.009 ± 0.003

[a] In 80% v/v EtOH–$\mathrm{H_2O}$ with 0.90 *M* perchloric acid at 1°. [b] Ratio of reactants in starting mixture. [c] Extrapolated to zero time. Errors quoted represent observed scatter; calculated uncertainty ±10%; minimum absolute error ~0.01. [d] Denominator ([halide] + [$\mathrm{Cr^{III}Hal^{2+}}$]) equated to 2[dibromide]. [e] At 24°. [f] Denominator ([halide$^-$] + [$\mathrm{CrHal^{2+}}$]) equated to 2[$\mathrm{C_2H_4}$]. [g] Only results for peroxide addition to chromous solution included; inverse addition gave poorer reproducibility. [h] Results not affected by order of mixing.

In the reductive elimination of *trans*-1,2-dibromocyclohexane the amount of bromide ion did not increase linearly with $\mathrm{Cr^{II}}$ but leveled off at approximately 0.35. Styrene dibromide produced styrene quantitatively with $\mathrm{Cr^{II}}$ and reacted more than 200 times faster than the *trans*-cyclohexane analog. The amount of bromide released in reduction also leveled off at a lower value (0.15).

Reductive elimination of β-bromopropionyl peroxide with $\mathrm{Cr^{II}}$ was very rapid (5 min) at 0° in ethanol. Ethylene and carbon dioxide were produced quantitatively according to eq 11. Under these conditions,

$$\mathrm{(BrCH_2CH_2CO_2)_2 + 2Cr^{II} \longrightarrow H_2C{=}CH_2 + CO_2 + [Cr^{III},Br^-] + Cr^{III}O_2CCH_2CH_2Br} \qquad (11)$$

correction for the catalyzed solvolysis of $\mathrm{Cr^{III}Br}$ was negligible even in the presence of excess $\mathrm{Cr^{II}}$. The relative amount of free bromide in this case also was dependent on the $\mathrm{Cr^{II}}$. At high $\mathrm{Cr^{II}}$, it leveled off at 0.30, a value which is in striking agreement with that obtained from *trans*-1,2-dibromocyclohexane.

The chlorine analog of the bromoacyl peroxide also reacted rapidly with $\mathrm{Cr^{II}}$ at 0°. Ethylene, carbon dioxide, and $\mathrm{Cr^{III}Cl}$ were produced quantitatively accord-

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(15) An alternative explanation of this anomaly may be attributed to a $\mathrm{Cr^{II}}$ or $\mathrm{Cr^{III}}$ induced solvolysis of allyl bromide.

(16) D. Pennington and A. Haim, *J. Am. Chem. Soc.*, **88**, 3451 (1966).

ing to eq 12. Significantly, only traces of free chloride ion were produced.

$$(ClCH_2CH_2CO_2)_2 + 2Cr^{II} \longrightarrow H_2C{=}CH_2 + CO_2 + Cr^{III}Cl + Cr^{III}O_2CCH_2CH_2Cl \quad (12)$$

Alkylchromium Compounds as Intermediates in Reductive Elimination. The formation of benzyl- and alkylchromium compounds as intermediates in the reduction of organic monohalides by Cr^{II} was reported earlier.[4,15] The analogous β-haloalkylchromium compounds are also possible intermediates in the stepwise removal of halogens in reductive elimination of 1,2-dihaloalkanes.

A kinetic examination for such a metastable intermediate did not prove to be a sufficiently sensitive probe. Thus, the first-order rate of disappearance of 1,2-dibromocyclohexane (by gas chromatography) coincided with the first-order appearance of cyclohexene (by gc). The rates of disappearance of Cr^{II} and 1,2-dibromocyclohexane were also in reasonable agreement.

Organochromium compounds exhibit an absorption band (*vide infra*) in the visible region[1c,4] and spectral studies were carried out to scrutinize further any evidence of such an organochromium species. The visible spectra of solutions of Cr^{II} and halides in DMF were repeatedly scanned for changes in absorption. Three substrates were investigated: *cis*-1,2-dibromocyclohexane, iodocyclohexane, and *t*-butyl iodide. Only the last named showed evidence of an intermediate under these conditions. Iodocyclohexane reacted rather slowly with Cr^{II} and the cyclohexylchromium was only observed when the more potent Cr^{II}en reductant was used. Failure to observe organochromium intermediates in the reduction of dibromocyclohexane and iodocyclohexane was probably due to their rate of reaction being in excess of their rate of formation.

Two isosbestic points were observed at 765 and 675 $m\mu$ for reaction of iodocyclohexane and Cr^{II}. The absorption maxima at 585 and 412 $m\mu$ increased at parallel rates. Similarly, isosbestic points were observed at 765 and 690 $m\mu$ for *cis*-1,2-dibromocyclohexane and the rates of increase of the maxima at 590 and 415 $m\mu$ were the same. These trends were attributed to the halochromium(III) and Cr^{III} species.[17] However, *t*-butyl iodide exhibited different spectral behavior with Cr^{II}. Isosbestic points at 760 and 675 $m\mu$ were noted, but the maximum at 420 $m\mu$ was observed to build up and then decay. The absorbance at 425 $m\mu$ is plotted against time in Figure 3. The metastable species is undoubtedly *t*-butylchromium analogous to those alkylchromium compounds observed in reduction of alkyl halides with Cr^{II}en.[4]

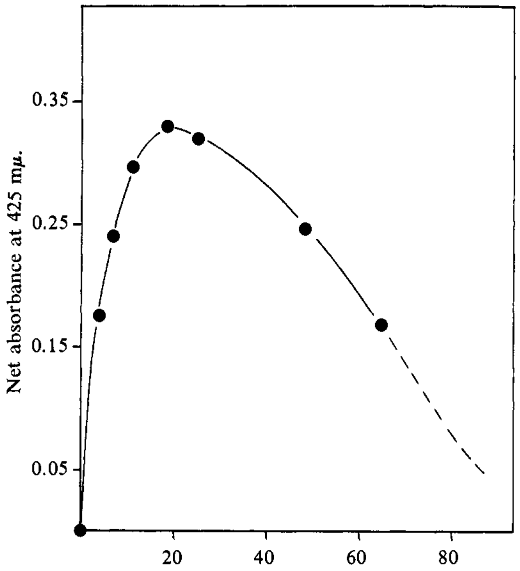
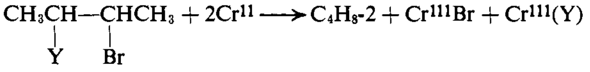


Figure 3. Appearance and decay of the metastable *t*-butylchromium ion from *t*-butyl iodide and 1.3 × 10^{-3} *M* Cr^{II} perchlorate in DMF.

$$(CH_3)_3CI + 2Cr^{II} \longrightarrow (CH_3)_3CCr^{III} + Cr^{III}I \quad (13)$$

We conclude from these studies that β-haloalkylchromium species, if intermediates in reductive elimination, are too unstable to be detected kinetically.

Effect of β Substituents on Rates of Reductive Elimination. In addition to vicinal dihalides, a variety of other β-substituted alkyl halides undergo reductive elimination with Cr^{II}.[7b,8] In order to determine the effect of substituents other than bromine, we examined the rates of reduction of 3-substituted 2-bromobutanes. Butene-2 was formed in each case and the second-order



$$\underset{\textstyle Y}{CH_3CH}{-}\underset{\textstyle Br}{CHCH_3} + 2Cr^{II} \longrightarrow C_4H_8\text{-}2 + Cr^{III}Br + Cr^{III}(Y) \quad (14)$$

rate constants from the *threo* and *erythro* pair was compared in Table VI with *sec*-butyl bromide.

Table VI. Reductive Elimination of 3-Substituted 2-Bromobutanes by Cr^{II} [a]

3-Y-2-Bromobutane, Y	Concn,[b] *M*	$k_2 \times 10^4$, l. mole^{-1} sec^{-1}	Relative rate
H	0.043[c]	0.14 ± 0.01	0.07
dl-erythro-3-Hydroxy	0.033[d]	0.65 ± 0.07	0.3
dl-threo-3-Hydroxy	0.033[d]	0.68 ± 0.15	0.3
dl-erythro-3-Acetoxy	0.033	2.1 ± 0.1	1.0
dl-threo-3-Acetoxy	0.033	2.0 ± 0.2	1.0
dl-erythro-3-Tosyloxy	0.051	7.7	4
dl-threo-3-Tosyloxy	0.044	6.0	3
dl-erythro-3-Chloro	0.033	51 ± 1	25
dl-threo-3-Chloro	0.033	25 ± 0	12
meso-3-Bromo	0.013	1600	780
dl-3-Bromo	0.013	660	320

[a] In 85% DMF containing 5% water, 10% ethanol, and 0.90 *M* perchloric acid and 0.057 *M* Cr^{II} at 0°. [b] Rate constants also determined at 0.012 *M* 3-Y-2-bromobutane. [c] Followed to 10% completion only, second-order kinetics assumed. [d] Followed to 20% completion only.

Discussion

Reductive elimination of *vic*-dihalides by Cr^{II} to alkenes exhibits characteristics similar to the reduction of alkyl monohalides to alkanes by the same reagent. The rates of reduction of both are significantly enhanced on going from ethanol to DMF solvent and by the addition of ethylenediamine to complex Cr^{II}. The order of halogen reactivity is I > Br > Cl in both reactions. The Cr^{III} species produced from alkyl halides (X) is $Cr^{III}X$ and at least one halogen from reductive elimination of dihalides is converted into the same $Cr^{III}X$ species.

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[17] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

The mechanism of reduction of alkyl halides has been shown to proceed *via* a multistep sequence consisting of 1-equiv oxidation–reduction reactions. The mechanism given by eq 15–17 was proposed.[1]

$$\mathrm{RX} + \mathrm{Cr^{II}} \longrightarrow \mathrm{R\cdot} + \mathrm{Cr^{III}X} \tag{15}$$

$$\mathrm{R\cdot} + \mathrm{Cr^{II}} \longrightarrow \mathrm{RCr^{2+}} \tag{16}$$

$$\mathrm{RCr^{2+}} + \mathrm{SH} \longrightarrow \mathrm{RH} + \mathrm{Cr^{III}(S)} \tag{17}$$

Alkyl radicals are formed in an initial ligand transfer[1,18a] of halogen from the alkyl group to $\mathrm{Cr^{II}}$. The subsequent association (eq 16) of the free radical with $\mathrm{Cr^{II}}$ is fast.[18b] In most cases the heterolysis of the alkylchromium to alkane (eq 17) is also rapid compared to the first step. Solvolytic stability of alkylchromium compounds decreases in the order benzyl > *t*-alkyl > *sec*-alkyl > primary alkyl. It is thus not surprising that alkylchromium species as intermediates in the reaction of alkyl halides and $\mathrm{Cr^{II}}$ have heretofore been observed only with benzylic halides and *t*-butyl iodide.

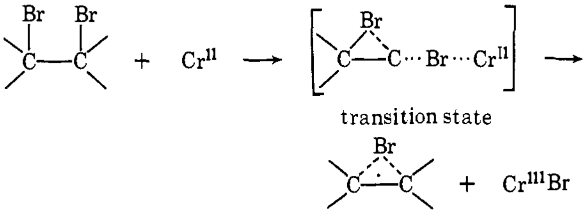
Diacyl peroxides and alkyl hydroperoxides are reduced by $\mathrm{Cr^{II}}$ very much faster than organic halides. An analogous mechanism involving oxygen–oxygen bond fission and transfer of a carboxylato or hydroxo ligand to $\mathrm{Cr^{II}}$ has been presented[8] and is given by eq 18, 19, and 16.

$$\mathrm{(RCO_2)_2} + \mathrm{Cr^{II}} \longrightarrow \mathrm{RCO_2\cdot} + \mathrm{Cr^{III}O_2CR} \tag{18}$$

$$\mathrm{RCO_2\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{CO_2} \tag{19}$$

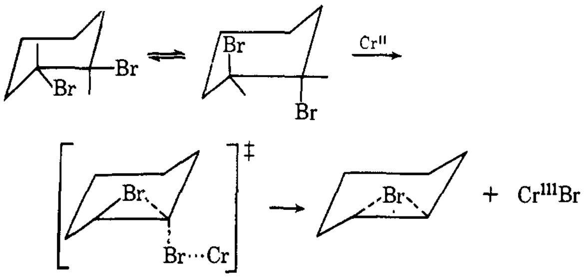
$$\mathrm{R\cdot} + \mathrm{Cr^{II}} \longrightarrow \mathrm{RCr^{2+}} \quad \text{etc.} \tag{16}$$

Removal of the First Halogen. Reductive elimination of *vic*-dihalides by $\mathrm{Cr^{II}}$ must also be a multistep reaction since the stoichiometry of the activation process is of a lower order than that of the over-all reaction. Similarity to reduction of alkyl halides and peroxides is maintained if the initial reaction is considered as a ligand transfer process to generate a β-haloalkyl radical. We follow Kray and Castro[7b] in attributing the enhanced rate of reduction of *vic*-dihalides compared to alkyl halides to a neighboring group effect by a β-bromo substituent.



(20)

It is difficult to attribute the hundred-odd fold greater rate of reduction of *trans*-1,2-dibromocyclohexane compared to the *cis* isomer to factors other than stereochemical differences. The *cis* isomer maintains the halogen substituents on the cyclohexane ring in an axial-equatorial disposition. It has been shown that *trans*-1,2-dibromocyclohexane exists as an equilibrium mixture of diaxial and diequatorial conformers in an essentially equimolar proportion.[19,20] Neighboring group assistance is optimum when groups are arranged in a transoid configuration, which is only possible in the *trans* isomers in cyclohexane systems.[21] If the population of the less reactive conformer is taken into account, the rate of diaxial *trans*-1,2-dibromocyclohexane will be several hundred times more reactive than that of the *cis* isomer.[22] Furthermore, the low activation energy for the *trans* isomer given in Table IV is only slightly affected by the small enthalpy change in the preequilibrium step between diaxial and diequatorial conformers.[20]



(21)

Neighboring group participation by bromine in homolytic reactions of bromocyclohexanes has been elegantly established by Skell and co-workers.[23] The concept was originally proposed by Goering to account for the stereospecific homolytic addition to 1-bromocyclohexene.[24] The effect diminishes with neighboring chlorine[25] and is even less with hydroxy and acetoxy. In acyclic systems Kray and Castro[7b] found that chlorine is not as effective as bromine as a neighboring group in reductive eliminations. The data in Table VI also show that bromine is a much more effective neighbor than chlorine, tosylate, hydroxyl, or acetoxyl in reductive eliminations in the butane system. The order of effectiveness of hydroxy and acetoxy compared to bromine as neighboring groups in homolytic reactions contrasts with their reactivity in intramolecular nucleophilic reactions.[26]

In iodide-induced[27] and zinc-promoted[28a] reductive eliminations of β-substituted alkyl bromides, a β-tosyloxy group is at least as effective as a β-bromo substituent. This behavior has been used to rationalize mechanisms for these two processes which involve a concerted ionic elimination (transoid transition state).[27,28] Contrariwise, in chromous-induced eliminations, as shown in Table VI, a β-tosyloxy group is much *less* effective than a neighboring bromine and only slightly more effective than β-acetoxyl in promot-

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(18) (a) J. Kochi and R. Subramanian, *J. Am. Chem. Soc.*, **87**, 1508 (1965). (b) Reaction of $\mathrm{Cr^{II}}$ ($3d^4$) and free radicals like the dimerization of radicals is probably close to diffusion controlled, since substitution in $\mathrm{Cr^{II}}$ is so facile:[8] T. Swift and R. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

(19) O. Hassel, *Research*, **3**, 504 (1950); *Tidsskr. Kjemi Bergvesen Met.*, **6**, 96 (1946).

(20) P. Bender, D. Flowers, and H. Goering, *J. Am. Chem. Soc.*, **77**, 3463 (1955).

(21) An argument based on the "diaxial rule" [D. Barton, *J. Chem. Soc.*, 1027 (1953)] by microscopic reversibility: P. Skell and P. Readio, *J. Am. Chem. Soc.*, **86**, 3334 (1964).

(22) (a) Provided axial attack is not significantly preferred to equatorial attack by free radicals: *cf.* G. Russell, A. Ito, and R. Konaka, *ibid.*, **85**, 2988 (1963); (b) F. Greene, C. Chu, and J. Walia, *J. Org. Chem.*, **29**, 1285 (1964).

(23) P. Skell, Special Publication No. 19, The Chemical Society, London, 1965, p 131. See, however, W. Haag and E. Heiba, *Tetrahedron Letters*, 3683 (1965).

(24) H. Goering, P. Abell, and B. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952); B. Bohm and P. Abell, *Chem. Rev.*, **49**, 599 (1962); P. Abell and L. Piette, *J. Am. Chem. Soc.*, **84**, 916 (1962).

(25) W. Thaler, *ibid.*, **85**, 2607 (1963); P. Skell, D. Tuleen, and P. Readio, *ibid.*, **85**, 2849 (1963); A. Ash and H. Brown, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **9**, 81 (1948); P. Fredericks and J. Tedder, *J. Chem. Soc.*, 144 (1960).

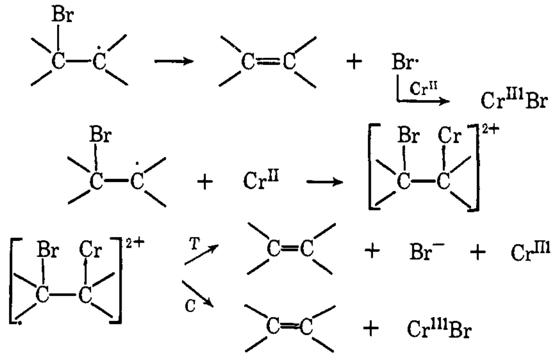
(26) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 141ff.

(27) S. Cristol, J. Weber, and M. Brindell, *J. Am. Chem. Soc.*, **78**, 598 (1956).

(28) (a) S. Cristol and L. Rademacher, *ibid.*, **81**, 1600 (1959); (b) H. House and R. Ro, *ibid.*, **80**, 182 (1958).

ing the transfer of the initial bromine to $\mathrm{Cr^{II}}$. This is in accord with the postulation of a homolytic transition state in chromous reductions, since a β-tosyloxy group, like acetoxy and hydroxy, is not expected to provide as substantial a driving force as an adjacent bromine substituent.

Removal of the Second Halogen. The formation of free bromide ion is associated with the removal of the second halogen atom. The amount of free bromide generated in reductive elimination of *vic*-dibromides and β-bromoacyl peroxides increases with $\mathrm{Cr^{II}}$ and at high $\mathrm{Cr^{II}}$ reaches a plateau which is characteristic of the alkyl moiety (Table V). We can accommodate these data if we postulate that the removal of the second halogen proceeds *via* several competitive routes. Thus, alkene is produced from a β-bromoalkyl radical[29] *via* three simultaneous reactions given by eq 22, 23, and 24.



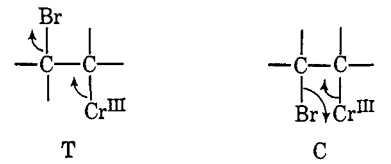
(22)

(23)

(24)

In this scheme, the first-order fragmentation of the β-bromoalkyl radical (eq 22) competes with a second-order reaction with $\mathrm{Cr^{II}}$ (eq 23). Bromine atoms formed in the fragmentation are known to react with $\mathrm{Cr^{II}}$ rapidly to produce $\mathrm{Cr^{III}Br}$.[17,30a]

We attribute the variation in free bromide with $\mathrm{Cr^{II}}$ to a second-order reaction between the β-bromoalkyl radical and $\mathrm{Cr^{II}}$ to produce a β-bromoalkylchromium transient. Although this intermediate has not yet been identified spectrally or kinetically, we are encouraged to present it in analogy with previous studies on alkyl halides. Alkene is formed by two alternative modes of heterolysis of this species. Free bromide and $\mathrm{Cr^{III}}$ are ejected from the β-bromoalkylchromium intermediate by one path (eq 24T)[30b] and $\mathrm{Cr^{III}Br}$ is synchronously eliminated in a *cis* fashion in another (eq. 24C). The transition states for these two competing processes can be formulated as



T C

The transition states for *trans* (T) and *cis* (C) elimination of β-substituted alkylchromium intermediates.

The relative rates of alkene formation from bromoalkyl radical and $\mathrm{Cr^{II}}$ are dependent on the structure of the β-haloalkyl moiety. Studies in Table V indicate that eq 24T is favored over eq 24C by a factor of 2 in the β-bromocyclohexyl and β-bromoethyl moieties. In the more stabilized α-phenyl-β-bromoethyl intermediate derived from styrene dibromide the relative rates are reversed and eq 24C is more facile than eq 24T. The increase importance of a concerted *cis* elimination in the benzylic system can be attributed to the importance of conjugation between the incipient double bond and the aromatic ring in the transition state. The difference between *cis* and *trans* elimination may also be partly due to the degree of rupture or ionic character of the C–Cr bond in the transition state. A similar description has been presented for *cis* elimination in the base-catalyzed E2 reaction by Froemsdorf.[31]

The most important factor which governs *cis* elimination (eq 24C and structure C) from the β-bromoalkylchromium intermediate is the driving force derived from the formation of a halogen bond to $\mathrm{Cr^{III}}$.[32] This process is more important with a β-chloroalkyl moiety than the bromine analog as shown by the absence of free chloride in the former. Preliminary studies indicate that neighboring hydroxy, acetoxy, and amino groups are also eliminated by a concerted *cis* elimination to yield a hydroxy-, acetoxy-, or amino-complexed $\mathrm{Cr^{III}}$ species.[33] The *cis* elimination of these groups is also aided by the unfavorable competing reactions in which the β-substituted alkyl radical undergoes homolytic fission (eq 22) or reaction with $\mathrm{Cr^{II}}$ to release chloride, acetate, hydroxide, or amide ions.

With the exception of bromine, of the β substituents examined a tosyloxy group is most likely to be removed from the alkylchromium intermediate *via trans* elimination (eq 24T, structure T). An analogous explanation has been presented for iodide- and zinc-promoted eliminations,[27,28] and it is consistent with tosylate ion as a particularly effective leaving group in ionic reactions.[34] The fragmentation of a β-tosyloxyalkyl radical (*cf.* eq 22) is a highly unlikely route to alkene formation.

Attempts to trap the intermediate β-haloalkyl radical have not been successful. Reduction of dibromocyclohexane in ethanol and DMF always yields a small amount of bromocyclohexane which may be derived from a β-bromocyclohexyl radical. Reactions carried out in allyl alcohol as solvent were not substantially different from those in ethanol or DMF. However, Barton has recently reported that similar intermediates can be trapped with mercaptans and 1,4-cyclohexadiene.[35,36] From previous studies we expect alkyl free

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[29] In subsequent discussions we will not distinguish between reactions of a bridged or an open β-bromoalkyl radical. This point will be discussed later in connection with the over-all stereochemistry of the reductive elimination process.

[30] (a) G. Gordon and R. Thompson, *Inorg. Chem.*, **5**, 559, 562 (1966). (b) It is, of course, also possible that bromide is formed directly from a simple second-order reaction between $\mathrm{Cr^{II}}$ and a β-bromoalkyl radical without the intervention of an alkylchromium intermediate. The bromide-forming reaction must, however, include $\mathrm{Cr^{II}}$.

[31] D. Froemsdorf, W. Dowd, and K. Leimer, *J. Am. Chem. Soc.*, **88**, 2346 (1966).

[32] At this stage nothing is implied about the stereochemistry of the over-all elimination, which will be limited by the stereochemical integrity of a free-radical intermediate. We hope to discuss this point further at a later time.

[33] L. Andrews, unpublished studies. Anet and Isabella first noted reductive elimination of β-bromoamines and alcohols by chromous chloride (*Can. J. Chem.*, **36**, 589 (1958)).

[34] The effect of leaving groups on the over-all stereochemistry of reductive eliminations in 3-substituted 2-halobutanes (*cf.* Table VI) will be discussed later.

[35] (a) D. Barton, N. Basu, R. Hesse, F. Morehouse, and M. Pecht, *J. Am. Chem. Soc.*, **88**, 3016 (1966). These results, however, are not unequivocal evidence of radical trapping since it is possible that an alkylchromium species will also be reduced by these agents. (b) Trapping of such intermediates is optimum in dimeric chromous acetate systems,[8,36] presumably due to low concentrations of $\mathrm{Cr^{II}}$.

[36] J. Kochi and R. Subramanian, *Inorg. Chem.*, **4**, 1527 (1965).

radicals to react with Cr^{II} in close to a diffusion-controlled rate and it may be indicative of our lack of success in trapping the radical intermediate by conventional means.[35b]

The fragmentation of a β-bromoalkyl radical to bromine atoms and alkenes (eq 22) is well known to be facile.[37] For example, the activation energy for dissociation of bromine from β-bromoethyl radical has been estimated to be 7 kcal/mole.[38] Similarly the fragmentation of β-bromoisobutyl radical has been estimated from bond energy data to be exothermic by 5 kcal/mole.[39,40] In our studies Cr^{II} can effectively obviate the fragmentation reaction when it is simply employed in excess. This provides further support for the efficiency of Cr^{II} as a free-radical trap in reduction, much like Cu^{II} in an oxidation capacity.[41]

Cr^{II} as a Reductant. The reactivity of Cr^{II} as a reagent for reduction of alkyl halides is markedly dependent on its ligands. Carboxylato Cr^{II} compounds are highly dimeric and diamagnetic and are generally the least reactive Cr^{II} reductants. If they can be compared to carboxylato Cu^{II} species,[36] it is only the monomeric species which are ligand transfer agents. Halides also suppress reactivity of Cr^{II} due to complex formation.[42] The effect compared to $Cr^{II}(H_2O)_6$ or $Cr^{II}(EtOH)_6$ is not large but measurable qualitatively. The use of nitrogen ligands promotes Cr^{II} as a reducing agent. Thus, DMF is preferred to ethanol as a solvent and can also be used in dilute solutions of the latter to enhance reactivity. Strongly coordinating ligands such as ethylenediamine and ethanolamine appear to have the largest enhancing effect on Cr^{II}. Under these conditions reductive elimination of dichlorides and even chloro alcohols and amines is extremely facile at ambient temperatures. The mechanism of reduction by these complex Cr^{II} reagents appears to be similar to uncomplexed Cr^{II}.

Summary and Conclusions

Reductive elimination of *vic*-dihalides by Cr^{II} to alkenes proceeds *via* a multistep sequence (eq 20, 22, 23, and 24). Stereochemical studies with *cis*- and *trans*-1,2-dibromocyclohexanes show that a β-bromine substituent is an effective neighboring group for removal of halogen by ligand transfer to Cr^{II}. Alkene is formed *via* three competing processes. The resulting β-bromoalkyl radical spontaneously ejects a bromine atom to liberate alkene or in a competing reaction with Cr^{II} forms a β-bromoalkylchromium intermediate. The former route can be minimized by use of excess Cr^{II} reagent. The β-bromoalkylchromium species is subsequently partitioned between *cis* or *trans* elimination of $Cr^{III}Br$ or bromide and Cr^{III} to form alkene. Each of these paths are important alkene-forming reactions from *vic*-dibromides or β-bromoacyl peroxides and Cr^{II}. The mechanism of reductive elimination of the related β-chloro-, -hydroxy-, and -acetoxybromoalkanes is less complex since fragmentation of the intermediate radical and *trans* elimination of the alkylchromium species are less important reactions.

Experimental Section

Materials. *trans*-1,2-Dibromocyclohexane was purchased from Columbia Organic Chemicals Co. It was washed with sodium hydroxide solution, then water, dried over sodium sulfate, and distilled: bp 86–87° (5 mm); $n^{20}D$ 1.5499 (lit.[43] bp 115–117° (28 mm); $n^{25}D$ 1.5495).

cis-1,2-Dibromocyclohexane was synthesized by the method of Goering:[44] bp 78.0–78.2° (1.8 mm); $n^{20}D$ 1.5515 (lit.[44] bp 50.5–51.5° (0.13 mm); $n^{20}D$ 1.5509). The infrared spectrum showed sharp peaks at 7.69, 8.27, 10.23, and 12.12 μ (lit.[45] 7.70, 8.23, 10.20, and 12.02 μ). Peaks corresponding to the *trans* isomer at 10.00, 11.90, and 14.64 μ and to 1,1-dibromide at 11.35 and 14.20 μ were absent. The starting material, 1-bromocyclohexene, was synthesized by the method of Stevens,[46] bp 56.5–57.2° (21 mm) (lit.[46] bp 63° (20 mm)).

Bromocyclohexane was obtained from City Chemical Corp.: specified bp 46–47° (10 mm); $n^{26}D$ 1.4947 (lit.[43] $n^{15}D$ 1.4956). Glc analysis (9 ft DEGS–Firebrick at 126°) indicated homogeneity (>99.5% pure). It was used without further purification. Iodocyclohexane was Eastman White Label; it was clear and colorless and was used directly.

t-Butyl iodide was Eastman White Label. It was washed with sodium bisulfite solution and then water, then dried over sodium sulfate and distilled, bp 43–44° (50 mm) (lit.[43] bp 20.8° (30 mm)). The material rapidly turned brown so it was treated with solid $Na_2S_2O_3$, decanted, and stored over anhydrous K_2CO_3, $n^{25}D$ 1.4881 (lit.[43] $n^{20}D$ 1.4918).

Styrene dibromide was prepared by the addition of bromine to a solution of freshly distilled styrene in ether at −10°. The product precipitated and was washed with chilled ether before being crystallized from ethanol, mp 72.5–73.0° (lit.[7b] mp 71.5°).

3-Bromopropionyl chloride was prepared by mixing 3-bromopropionic acid (Eastman White Label) with a slight excess of thionyl chloride (purified according to the method of Fieser[47]) and stirring at 40° for 20 hr (sluggish reaction). The mixture was distilled through an 8-cm glass helices packed column, bp 44.0–44.5° (7 mm) (lit.[48] bp 65–67° (25 mm)). Bis(3-bromopropionyl) peroxide was prepared according to the method of Kochi. It had a melting point of 39.0–39.4°, the infrared spectrum (in $CHCl_3$) showed a clear doublet at 5.51 and 5.61 μ (the 5.85-μ region was clear), and iodometric titration showed 99.4% purity.

Bis(3-chloropropionyl) peroxide was prepared in an analogous fashion, using 3-chloropropionyl chloride (Eastman White Label) which had been distilled through an 8-cm glass helices packed column, bp 31–32° (7 mm) (lit.[43] bp 143–145° (763 mm)). The infrared spectrum ($CHCl_3$ solution) of the peroxide showed a well-resolved doublet at 5.51 and 5.61 μ. Iodometric titration indicated a purity of 101%.

Ethanol (Commercial Solvents, gold label, 95%) was purified by distillation from a trace of H_2SO_4 through a 2-ft Oldershaw column, a center cut being used. Dimethylformamide (Du Pont; specified distillation range 0.6°) was used without further purification.

Perchloric acid was 70–72% ANALAR material from Matheson Scientific or Baker and Adamson and was used as received.

Allyl alcohol was Eastman White Label or Shell technical material. It was refluxed over anhydrous potassium carbonate, then distilled through a 2.5-ft glass helices packed column. A fraction boiling at 96.9–97.1° was used (lit.[43] bp 97°).

Ferric chloride (hexahydrate) was ANALAR material from Mallinckrodt. A fresh bottle was used and care was taken to ensure that at no time did it come into contact with metal (*e.g.*, spatulas). Potassium dichromate (Fisher Certified Reagent) was

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[37] M. Kharasch, J. Mansfield, and F. Mayo, *J. Am. Chem. Soc.*, **59**, 1155 (1937); H. Steinmetz and R. Noyes, *ibid.*, **74**, 4141 (1952); *cf.* also N. Neureiter and F. Bordwell, *ibid.*, **82**, 5354 (1960).

[38] R. Barker and A. Maccoll, *J. Chem. Soc.*, 2839 (1963); P. Abell and R. Anderson, *Tetrahedron Letters*, 3727 (1964).

[39] W. Haag and E. Heiba, *ibid.*, 3683 (1965).

[40] The relative rate of fragmentation of β-bromoisobutyl radical and chlorine atom transfer from *t*-butyl hypochlorite has been determined as 6.3.[39] The latter is a facile reaction and determination of its rate constant enables an estimation of the rate of fragmentation of the β-bromoalkyl radical [D. Carlsson, J. Howard, and K. Ingold, *J. Am. Chem. Soc.*, **88**, 4726 (1966); C. Walling and V. Kurkov, *ibid.*, **88**, 4728 (1966)].

[41] J. Kochi and R. Subramanian, *ibid.*, **87**, 4055 (1965).

[42] Complex formation with chloride ion also causes a decrease in the reduction potential of Cr^{II}.[13]

[43] "Handbook of Chemistry and Physics," 45th ed., The Chemical Rubber Co., Cleveland, Ohio, 1964.

[44] H. Goering, R. Abell, and B. Aycock, *J. Am. Chem. Soc.*, **74**, 3588 (1952).

[45] H. Goering and L. Sims, *ibid.*, **79**, 6270 (1957).

[46] C. Stevens and J. Valicenti, *ibid.*, **87**, 838 (1965).

[47] L. Fieser, "Experiments in Organic Chemistry," 3rd ed, D. C. Heath Co., Boston, Mass., 1955, p 345.

[48] R. Dahlbom, *Acta Chem. Scand.*, **7**, 875 (1953).

dissolved in distilled water and standardized iodometrically by the method of Vogel.[49] Chromous perchlorate was prepared as before.[1c]

Silver nitrate solution was prepared from an ACCULUTE capsule (Anachemica Corp.), diluted to 10^{-3} N with distilled water, and standardized potentiometrically against a standard solution of potassium bromide prepared in the following manner. Potassium bromide (Baker Analyzed Grade) was dried at 110° for 12 hr and cooled in a desiccator, and a sample was accurately weighed and dissolved in distilled water so as to produce an approximately decinormal solution. A portion of this solution was diluted to $\sim 10^{-3}$ N with distilled water. Ceric sulfate solution was prepared from ceric ammonium sulfate (G. F. Smith Chemical Co.) and standardized by the method of Vogel.[50] Distilled water was obtained from bulk distillation in a tin-lined still.

Titrimetric Techniques. Chromous ion was determined by quenching aliquots in 80 ml of degassed quenching solution (10 g of $FeCl_3 \cdot 6H_2O$, 400 ml of 10 M HCl, 1600 ml of water) and titrating the liberated ferrous ion with standard potassium dichromate in a nitrogen atmosphere. The titration flask used in this procedure was constructed by blowing side arms onto a 125-ml erlenmeyer flask so that the electrodes were immersed in the solution but were kept clear of the magnetic stirring bar by use of rubber sleeves which enabled depth of immersion to be adjusted. The solution was kept free of air by a constant stream of bubbling nitrogen.

The buret was a Sargent constant-rate buret of 10-ml capacity, used in conjunction with a pH recording adaptor and recorder (E. H. Sargent Co.). A platinum and a calomel electrode were used for this redox titration.

When a sample was to be analyzed, 80 ml of quenching solution was flushed with nitrogen in the titration flask, then an aliquot of sample was added by syringe. The recorder drive was activated and the buret delivery button was locked into place at the instant that the pen crossed a convenient chart line (this technique avoided errors due to mechanical time lag on starting the recorder chart drive). The curve traced was the typical sigmoid potentiometric curve and the end point was taken to be the center of the region of maximum slope. It was convenient to use a 1-in./min chart speed since the buret delivered at 1 ml/min; thus 1 in. of chart represented 1 ml. When titers greater than about 3 ml were required and when speed was important (*e.g.*, kinetics), it was found necessary to add part of the necessary potassium dichromate from a calibrated, graduated pipet and to add only the last 2–3 ml by buret. The entire system was tested with standard ferrous ammonium sulfate solution and the accuracy was found to be within the observed reproducibility (±0.05 ml, 0.01 N $K_2Cr_2O_7$).

Halide ion titrations were performed with similar apparatus except that the reagents and electrodes were changed and oxygen was no longer a problem so that a beaker was used as a titration flask. For these titrations the calomel electrode was protected by a potassium nitrate bridge and used in conjunction with a silver electrode. Reproducibility was ±0.15 ml of 10^{-3} N $AgNO_3$. It was established that addition of small amounts of ethanol, toluene, or dimethylformamide did not affect the end point.

Ion Exchange. Ion-exchange measurements were carried out using a 10–15 cm × 1 cm column of Dowex 50W-X12 resin (100–200 mesh) in the hydrogen form. Before use, the resin was washed, by decantation, with 10% NaOH, water, 1 M perchloric acid, and water. The column was surrounded by a jacket through which was circulated ice water. Under these conditions it was established that anions and monopositive cations were eluted by 200 ml of 0.1 M $HClO_4$, $CrBr^{2+}$ was eluted by 250 ml of 0.5 M $HClO_4$, and Cr^{3+} was eluted by 250 ml of 0.85 M $HClO_4$. Prolonged (2 hr) soaking with 1 M disodium hydrogen citrate was necessary to remove the binuclear complex formed when oxygen reacts with chromous ion.[51] The column was regenerated between runs by eluting successively with 1 M disodium hydrogen citrate, 1 M perchloric acid, and distilled water. The eluent was analyzed by treatment with alkaline hydrogen peroxide, dilution to known volume, and measurement of the absorption at 374 mμ (ϵ 4815).[52]

Kinetic Technique. Chromous solutions in the appropriate solvent and contained in a serum-capped erlenmeyer flask were equilibrated in a constant-temperature bath, then aliquots were withdrawn by nitrogen-flushed syringe for standardization. The requisite quantity of a degassed, standard solution of substrate was then added to the stirred mixture and timing commenced. Aliquots were withdrawn at intervals and titrated with standard $K_2Cr_2O_7$ by the method described above. Rate constants were calculated using the expression $k = [1/t(b - 2a)][\ln (a(b - 2x)/b(a - x))]$ and plotting $\ln [(b - 2x)/(a - x)]$ *vs.* t, where $k = \text{slope}/(b - 2a)$. Ionic strength and acidity effects were investigated using combinations of $LiClO_4$ and $HClO_4$, and LiCl was used to check the effect of chloride ion.

Product Studies. Measurement of organic products was performed by gas chromatography and yields were normally based on chromous ion consumed. For liquid products an internal marker was added to the reaction mixture and an aliquot was partitioned between a tenfold excess of water and 3 ml of toluene. The toluene layer was separated and washed once with water, then analyzed. Calibration factors were obtained by working up authentic mixtures in the same way. An Aerograph HiFy 600-D or A200 was used for analyses. For gaseous products Case-constructed chromatographs with thermal conductivity detectors were employed. Reactions were carried out in serum-capped erlenmeyer flasks which were degassed and stirred thoroughly. Products were sampled directly.

Inorganic products were measured by use of ion exchange and titration techniques described above. Reactions were carried out at 1° to minimize aquation of $CrBr^{2+}$ ions and were quenched by pumping in a large excess of pure oxygen and agitating. It was found that slow oxidation often led to spuriously high yields of dipositive chromium ions under our conditions. Analysis of tripositive chromium ions was obscured by ions produced during the quenching of excess chromous ion. Therefore, it was more convenient to obtain this information by titration of the bromide ion eluted by 0.1 N $HClO_4$. This fraction was stored in a freezer at −15° until titrated to minimize reduction of perchlorate ion to chloride. Aliquots for ion exchange were diluted tenfold with ice water before analysis since they usually contained up to 0.9 M $HClO_4$ which would cause poor and less than quantitative separation of species on the column. Arrangements were made to apply moderate (3–5 psi) pressures of nitrogen to the column when the flow rate was low.

It was found that the value obtained by titrating an aliquot of reaction mixture directly with silver nitrate at 0° agreed well with the value obtained for the 0.1 N acid eluent from ion exchange in cases where there was no unreacted alkyl halide. This technique was not applied when alkyl halide remained unconsumed.

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(50) See ref 49, p 302.

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(52) G. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).