ALKENES FROM HALIDES AND EPOXIDES BY REDUCTIVE ELIMINATIONS WITH Cr^{II} COMPLEXES

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Abstract—A variety of β -substituted alkyl halides and epoxides are reductively eliminated in high yields to alkenes by Crⁿen at room temperature. The reducing agent is easily prepared in situ from chromous salts and ethylenediamine. Reductive elimination and protolytic reduction of B-substituted alkyl halides by chromous reagent proceed by similar mechanisms, and involve free radicals and alkylchromium species as intermediates. In the former process, B-substituents such as hydroxy, phenoxy, acetoxy, tosyloxy, bromo, chloro, amino and trimethylammonium groups are readily eliminated from the β -substituted alkylchromium intermediate to generate alkene. Protolytic reduction of the alkylchromium species is a significant competing reaction only with such β -substituents as cyano, benzamido and phthalimido groups. Factors which determine the effect of groups on the relative rates of reductive elimination and protolytic reduction of the alkylchromium species are discussed. The formation of a free radical by an initial ligand transfer of halogen from the alkyl halide to chromous ion is enhanced by β-bromo and trimethylammonium groups. Neighboring group participation by these groups in homolytic processes to form bromine or trimethylammonium-bridged alkyl radicals as intermediates is postulated. Cr^{π} en is a more powerful reductant than Cr^{II} and the scale of relative reactivity of various halides is compressed in the former relative to the latter. *o*-Diiodobenzene is reduced by Cr^{il}en stepwise to benzene, and benzyne does not appear to be an intermediate in the reaction.

THE reductive elimination of vicinal dihalides can be represented by the process (half-reaction) given in Eq. 1. There are a number of reducing agents available for

$$\begin{array}{c} > C - C < + 2\varepsilon \rightarrow > C = C < + X^{-} + Y^{-} \quad X, Y = \text{halogen} \\ \downarrow \qquad \downarrow \\ X \quad Y \end{array}$$
(1)

1,2- or β -reductive elimination of vicinal dihalides to alkenes in good yields. Prominent among these is zinc,¹ followed by iodide salts, selenides,² phosphines,³ trialkylstannanes,⁴ Grignard reagent-metal salt,⁵ pentacyanocobaltate (II),⁶ lithium aluminium hydride,⁷ and a variety of other dehalogenating reagents. The subject has been reviewed recently.^{7,8}

In addition to vicinal dihalides, a variety of other β -substituted alkyl halides can also be reduced to alkenes (Eq. 1; X = halogen, Y = hydroxy, alkoxy, acyloxy, amino, etc). In such cases, metals or metal complexes such as zinc,⁹ magnesium¹⁰ or sodium¹¹ are the reducing agents of choice, and other reagents such as iodide and phosphines used in dehalogenations are much less effective. In general, yields of alkenes from these compounds are not as good as those from dibromides and dichlorides due to a competing reaction leading to protolytic reduction of only the carbon-halogen bond (Eq. 2). Hydroxide, alkoxide and amide are poor leaving groups,

in contrast to halides, and consequently alcohols, ethers and amines are often side products from reduction of β -halohydrins and their ethers and β -haloamines, respectively. Furthermore, these derivatives generally react significantly slower than the corresponding vicinal dibromides. Thus, β -bromohydrins and ethers require more than 5 hr of refluxing in aqueous ethanol with zinc or tetrahydrofuran with sodium to regenerate the parent alkenes in roughly 70% yields.¹¹ Similarly cyclohexene is formed from its bromohydrin, acetate and tosylate with zinc in refluxing ethanol or glacial acetic acid under comparable conditions.¹² The reductive elimination of β -chlorotriethylamine by sodium has been reported.¹³

Chromous salts were first employed by Julian et al.¹⁴ to effect reductive elimination of dihalides and α -keto-epoxides. This reaction has since been examined further¹⁵

to ascertain structural effects in the formation of alkenes from a variety of 1,2dihalides. Under rather vigorous conditions (refluxing aqueous solution), β -bromoethyl alcohol and amine react slowly with Cr^{II} to produce ethylene (Eq. 3; Y = HO, H₂N, X = Br) in poor yields, as well as ethyl alcohol and amine (cf. Eq. 2), respectively.¹⁶ Chloroethanol was not reduced under these conditions. In the presence of active hydrogen donors, the reduction of β -bromohydrins by Cr^{II} acetate can be modified to afford alcohols (cf. Eq. 4).¹⁷

Chromous salts can also be used to reduce organic monohalides. However, the reaction is practicable only with the more reactive α -haloketones¹⁸ and allylic as well

$$\mathbf{R} - \mathbf{X} + 2\mathbf{C}\mathbf{r}^{\mathrm{H}} + \mathbf{H}^{+} \rightarrow \mathbf{R}\mathbf{H} + 2[\mathbf{C}\mathbf{r}^{\mathrm{H}}, \mathbf{X}^{-}]$$
(4)

as benzylic halides.¹⁹ Simple alkyl halides generally are only slowly reduced to alkanes by this reagent. However, they can be readily reduced by a modified Cr^{II} reagent in which the chromous ion is complexed with ethylenediamine or related ligands.²⁰ Under these circumstances even the least reactive primary alkyl chlorides are readily reduced to alkanes at room temperatures.

The reactivity of halides with Cr^{II} reagents are in the relative order: t-alkyl > secalkyl > prim-alkyl (e.g., the ratio is 40:5:1 for alkyl bromides and Cr^{II} en in dimethylformamide).²¹ The reduction of organic iodides is faster than bromides or chlorides (relative reactivity is 7×10^3 : 5×10^2 :1 for n-butyl halides and Cr^{II} en in DMF, and 555:124:1 for benzyl halides and Cr^{II} in ethanol).²¹

The ability of simple (uncomplexed) Cr^{II} salts to reduce effectively only the more reactive epoxides and dihalides (bromides and iodides) limits their usefulness as general reagents for reductive eliminations. However, as a metal species, chromium should facilitate removal (*vide supra*) of hydroxide, alkoxide or amide from β -halo-hydrins, ethers and amines, respectively. The rate-limiting step in these reductions is the removal of the initial halogen atom.^{18, 19, 22} Since Cr^{II} en is a much more powerful reagent for abstracting halogen atoms than Cr^{II}, it combines all the attributes of an effective reagent for reductive elimination of a variety of compounds, expecially

^{*} In subsequent discussions, no attempt will be made to include the coordination around the chromous ion except when necessary for clarity. In aqueous DMF we will assumed octahedral coordination with DMF as well as water.

 β -substituted alkyl halides and epoxides. Furthermore, solubility of the Cr^{ll}en complex in a number of solvent systems lends it certain advantages over zinc in quantitative studies. In this report we have concentrated on derivatives of ethylene for study, since they are generally the least reactive in reductive eliminations. No doubt the scope of the reaction and our conclusions are also applicable to reductive elimination in other systems.

RESULTS AND DISCUSSION

Chromous salts are easily prepared in solution from chromic salts and $zinc^{23}$ or by dissolution of the pure metal in solutions of the appropriate acid according to Eq. 5.²⁴ The former method simultaneously introduces zinc ions, whereas the latter

$$Cr^{0} + 2HX \rightarrow Cr^{II}X_{2} + H_{2}$$
(5)

process yields only chromous salts and is amenable to actual isolation of crystalline compounds.²⁵ In our studies, the blue aqueous Cr^{II} solutions were simply diluted with dimethylformamide (DMF) and used as such. Since Cr^{II} reacts rapidly with oxygen all operations were carried on in the absence of air. This can be readily achieved by initially flushing the solvent in a flask equipped with a rubber serum cap with nitrogen, and then introducing an aliquot of a standard aqueous Cr^{II} solution by means of a hypodermic syringe. The purple Cr^{II} en reagent* was generated *in situ* by injecting a measured amount of ethylenediamine dissolved in DMF. The organic halide was then added, and the homogeneous reaction allowed to proceed at room temperature.

Reduction of β -substituted ethyl bromides. A series of β -bromoethyl compounds listed in Table I were reduced by Cr^{II}en under these conditions and the yields of ethylene determined by gas chromatography, using the internal standard method. The reactions were complete with all of these compounds within 15 min. Quantitative yields of ethylene were obtained from β -bromoethyl bromide, chloride, hydroxide, acetate, chloroformate, ethoxide, phenoxide and tosylate, as well as β -bromoethylamine and β -bromoethyltrimethylammonium salt. The azido and thiophenoxy derivatives gave less than quantitative yields of ethylene. The former underwent competitive reduction of the azido function, and the thioether may have undergone partial solvolysis. Cyanide and sulfite as leaving groups were poor. The compounds

$$BrCH_2CH_2CN + 2Cr^{Hen} \frac{DMF}{H_2O}CH_3CH_2CN + 2Cr^{Hen}(Br^{-})$$
(6)

reacted rapidly with Cr^{II}en reagent, but no ethylene was produced. Propionitrile was formed from the former quantitatively by protolytic reduction (Eq. 6).

Althouth β -bromoethylamine reacted rapidly with Cr^{II}en and produced ethylene in quantitative yields, the benzamido and phthalimido derivatives gave no ethylene. Only simple protolytic reduction of the Br—C bond occurred and N-ethyl benzamide and phthalimide, respectively, were produced.

Reduction of β -substituted ethyl chlorides. The β -chloroethyl analogues uniformly reacted with Cr^{II}en much slower than the β -bromoethyl compounds listed in Table 1.

[•] The Cr^{II}en reagent prepared by adding 2.9 moles of ethylenediamine to Cr^{II} in aqueous DMF is undoubtedly a mixture of mono-, di- and triethylenediamine chromium (II) cationic species. It probably consists mostly of Cr^{II}en₂ since the formation constants in water are: Cr^{II}en₁, log $K_1 = 5.15$; Cr^{II}en₂, log $K_2 = 4.04^{.26}$

BrCH ₂ CH ₂ Y ^b Y	Concentration (M)	Ethylene Yield (%)f
Bromo (Br)	0.025	Q
Chloro (Cl)	0-025	Q
Hydroxy (HO)	0.025	Q
Amino (H_2N)	0-025	Q
Chloroformoxy (ClCO ₂)	0-025	Q
Phenoxy (PhO)	0.010	0
r henoxy (r hO)	0.025	Q
Trimethylammonium [(Me ₃)N ⁺]	0-010	Q
Acetoxy (MeCO ₂)	0.013	Q
Ethoxy (EtO)	0-013	Q
p-Tosyloxy (TsO)	0.013	Q
Thiophenoxy (PhS)	0-013	34 ^d
	0-025	36 ^d
Azido (N.)	0.025	32e
	0-018	10 ^e
Cyano (NC)	0.013	<0·1 ^f
	0.025	< 0.1
Phthalimido (C.H.(CO), N)	0-025	<0.4
1 maaningo (06114(00)211)	0.010	< 0.3
Benzamido (PhCONH)	0-0052	<1·0
Sulfonato (TO-S)	0.013	<07
Sanonato (030)	0.025	<0.4

Table 1. Ethylene from the reduction of β -bromoethyl derivatives by Cr^{II}en^{*a*}

* In 10% v aqueous DMF containing 0-09M $Cr(ClO_4)_2$ and 0-20-0-24M ethylenediamine at room temp. All reactions complete in 15 min. Alkyl bromide added to Cr^{II} en soln.

^b All runs performed at least in duplicate.

 $^\circ$ Yields based on alkyl bromide. Q indicates yields quantitative (>95%) within experimental precision.

⁴ Competitive solvolysis may be important.

^e Side reaction liberating N_2 observed; butyl azide reduced by Cr^{ll} en with liberation of N_2 .

^f Propionitrile formed quantitatively (>99%).

In general, these chloro compounds required standing at room temperature overnight or longer for complete reaction. Yields of ethylene, however, were quantitative for β -chloroethyl chloride, hydroxide, acetate, phenoxide, methoxide and tosylate as well as β -chloroethylamine and tris- β -chloroethyl phosphite (Table 2). In the latter case, 3 moles of ethylene were generated with Cr^{II}en and each phosphite. On the other hand, β -chloroethyl nitrate afforded no ethylene due to facile reduction of the nitrato function. Ethylene was produced when a large excess of Cr^{II}en was employed.

Reduction of β -substituted diacyl peroxides. Ethylene and carbon dioxide were produced quantitatively from reaction of β -substituted propionyl peroxides and Cr^{II}, in which the substituents were bromine, chlorine or acetoxy. Diacyl peroxides

$$(YCH_2CH_2CO_2)_2 + 2Cr^{II} \rightarrow CH_2 = CH_2 + CO_2 + YCH_2CH_2CO_2Cr^{II} + Cr^{II}(Y^-)$$
(7)

CICH ₂ CH ₂ —Y ^b Y	Molarity (M)	Ethylene Yields (%)	
Chloro (Cl)	0-018	Q	
Hydroxy (HO)	0-025	Q	
Amino (H_2N)	0.025	Q	
Acetoxy (MeCO ₂)	0-025	Q	
Phenoxy (PhO)	0.025	Q	
p-Tosyloxy (TsO)	0.025	Q	
bis-Chloroethylphosphito [(ClCH ₂ CH ₂ O) ₂ PO]	0.008	Q ⁴	
Methoxy (MeO)	0.013	Q	
Nitrato (O ₂ NO)	0.018	<05	

TABLE 2. ETHYLENE FROM REDUCTION OF β -CHLOROETHYL DERIVATIVES BY Cr^{II}en^a

^a Alkylchloride added to Cr^{II} en soln. In 10%v aqueous DMF containing 0.09M CrII(ClO₄)₂, 0.20–0.24M ethylenediamine.

^b Runs performed at least in duplicate.

 $^{\circ}$ Yields based on alkyl chloride added. Q indicates quantitative within experimental precision (>95%).

⁴ Based on stoichiometry of 3 moles ethylene per mole of tris- β -chloroethyl-phosphite.

generally react readily with uncomplexed Cr^{II} at 0° without the aid of ethylenediamine.²⁸ The fate of the β -substituent can be easily determined quantitatively under these conditions by ion exchange chromatography of the reaction mixture. It is present (Table 3) either as the free anion (Y⁻) or complexed with Cr^{III} species as Cr^{III}Y. Hydrolysis of the latter is negligible under these conditions. β -Bromopropionyl peroxide yielded bromide ion (30%) and Cr^{III}Br ion (70%) at high Cr^{II} concentrations. Under the same conditions β -chloropropionyl peroxide produced only Cr^{III}Cl (100%) and no chloride ion.

(YCH ₂ CH ₂ CO ₂) ₂ Y	Peroxide (M)	Cr ^{II} (ClO ₄) ₂ (M)	Carbon dioxide (%) ^c	Ethylene (%) [¢]	Y- (%)⁴	Cr ^{III} Y+2 (%)4
Bromo (Br) ^b	0-006	0-023	100	100	30°	704
Chloro (Cl) ^b	0-010	0-063	100	100	<11	100*
Acetoxy (CH ₃ CO ₂)	0-013	0-075	100	100		

Table 3. Products from reduction of $\beta\text{-substituted bis-propionyl peroxides with } Cr^{II}(ClO_4)^a_2$

" Peroxide soln added to excess Cr^B. In EtOH solns at 0°.

^b Solns contain 1M perchloric acid to retard aquation of CrⁿⁱY.

^c All yields based on duplicate runs. Stoichiometry is 1 peroxide and 2 Cr^{n} form 1 carbon dioxide and 1 ethylene.

^d Sum of Y⁻ and Cr^{III}Y⁺² equal to 100%.

^e Bromide. ^f Chloride. ^e Bromochromic. ^h Chlorochromic.

Reduction of aryl and vinyl halides. Reduction of o-diiodobenzene with excess Cr^{II}en generated quantitative yields of benzene. The route to benzene, however, was not via reductive elimination to benzyne followed by further reduction of the acetylenic linkage.²⁹ When less than stoichiometric amounts of Cr^{II}en were employed, high

yields of iodobenzene were formed (Table 4). The stepwise protolytic reduction of o-diiodobenzene to iodobenzene, thence further reduction to benzene, is indicated



since Cr^{II}en reagent is capable of facile reduction of iodobenzene quantitatively to benzene under these conditions. Bromobenzene was readily reduced by Cr^{II}en to benzene, and vinyl bromide also afforded ethylene quantitatively. Chlorobenzene, however, was unreactive.

Substrate	Concentration (M)	Cr ^{II} (M)	Product (%)	Yield (%) ⁴
Vinyl bromide	0-013	0-10*	Ethylene	Q
Ethylene oxide	0-007	0-10 ⁶	Ethylene	Q
Bromobenzene	0-023	0-062°	Benzene	Q
p-Dibromobenzene	0-0086	0-062 ^c	Benzene	Q
Iodobenzene	0-022	0·062 ^c	Benzene	Q
o-Diiodobenzene	0-018	0-087°	Benzene	Q
o-Diiodobenzene	0-042	0-021*	Iodobenzene	> 80
Chlorobenzene,	0-025	0·062	Benzene	<04
Ethyleneimine ^e	0-022	0·10*	Ethylene	5
Cyclohexene oxide	0-014	0∙10	Cyclohexene	92 ^s
Styrene oxide	0-018	0.094	Styrene	Q
2-Fluoroethanol	0-013	0.10	Ethylene	12

TABLE 4. REDUCTION OF ORGANIC HALIDES AND EPOXIDES WITH Cr^{ll}en^a

^e In 10% v aqueous DMF at room temp. Substrate soln added to Cr^{il}en.

^b Ethylenediamine was 0.29M.

' Ethylenediamine was 0.67M.

^d Q indicates quantitative within experimental precision (>95%).

^e When en concentration raised to 0.60M, yield of ethylene decreases by approx. 50%.

^f Cyclohexanol not examined.

* Ethylenediamine was 0-18M. rapid reaction complete in 10 mins.

Reduction of epoxides. The reductive elimination of α_{β} -epoxyketones such as epoxides of mesityl oxide and benzalacetophenone by chromous chloride has been reported.³⁰ Similarly styrene epoxide reacted overnight with Cr^{II}Cl₂ to produce 80% (by spectral analysis) of styrene. The aliphatic cyclohexene oxide, however, produced mainly the adduct, cyclohexene chlorohydrin, with chromous chloride in HCl.

Under our conditions, Cr^{II} en reacted slowly with ethylene oxide to afford quantitative yields of ethylene. Similarly cyclohexene oxide produced good yields of cyclohexene with the reagent. The reduction of styrene oxide by Cr^{II} en was complete within a few minutes (Table 4).

The qualitative rates of reductive elimination of some of the less reactive substrates with Cr^{II} en are listed in Table 5. Comparative times for reaction are also given where available for reduction of similar compounds by uncomplexed Cr^{II} .

Substrate	Time (hr.)	Product	Conversion (%) ⁴	
(CICH ₂ CH ₂ O) ₃ P	12	Ethylene	93°	
	22	Ethylene	99	
CICH ₂ CH ₂ CI	1-0	Ethylene	82	
	1.25	Ethylene	93	
	2.0	Ethylene	Q	
PhI	< 0.1	Benzene	Q	
Cyclohexene oxide	48	Cyclohexene	73	
-	66	Cyclohexene	82	
	120	Cyclohexene	87	
	240	Cyclohexene	92	
meso-CH ₃ CHClCHClCH ₃ ^d	4 days	Butene-2	44	
PhI	3 days	Benzene	0	
PhBr ^e	3 days	Benzene	0	

TABLE 5. APPROXIMATE REACTIVITIES OF COMPOUNDS WITH Cr^{il}en⁴

• In solns of 10%v aqueous DMF; substrate, 0-013M; Cr^{II}, 0-09M; ethylenediamine, 0-24M at room temp.

^b Q indicates quantitative (>95%).

^c Based on 3 moles ethylene per mole substrate.

⁴ Ref. 19a. No ethylenediamine; Crⁿ, 015M, substrate 05M.

^e Ref 19b. No ethylenediamine; Cr^{II}, 0·25M, substrate, 0·03M.

Mechanism of reductive elimination by $Cr^{II}en$. The reduction of β -bromoethyl derivatives by $Cr^{II}en$ is complete within 15 min at room temperature regardless of whether reductive elimination (Eq. 3) or protolytic reduction (Eq. 4) occurred. Earlier it was shown that alkyl bromides and vicinal dibromides react with Cr^{II} by a two-step process.^{18–22} The initial step in the reduction sequence involves a homolytic transfer of a bromine atom to Cr^{II} (Eq. 8). The free radical intermediate I can

$$\frac{\text{YCH}_2\text{CH}_2 - \text{Br} + \text{Cr}^{11} \rightarrow \text{YCH}_2\text{CH}_2 + \text{Cr}^{11}\text{Br}}{\text{I}}$$
(8)

also be generated by the facile reaction of propionyl peroxides and Cr^{II} since decarboxylation of acyloxy radicals is rapid.³¹

$$(YCH_2CH_2CO_2)_2 + Cr^{II} \rightarrow YCH_2CH_2CO_2 \cdot + YCH_2CH_2CO_2Cr^{III}$$
$$YCH_2CH_2CO_2 \cdot \frac{\text{fast}}{I} YCH_2CH_2 \cdot + CO_2$$

We postulate that Cr^{II}en and Cr^{II} react with alkyl halides by the same mechanisms, and attribute the enhanced reactivity of Cr^{II}en to a more exothermic step (Eq. 9) involving halogen transfer.* This is supported by kinetic studies, which show a

$$YCH_2CH_2 - X + Cr^{II}en \rightarrow YCH_2CH_2 + Cr^{III}enX \qquad X = CI, Br \qquad (9)$$

smaller spread in reactivities of a series of β -substituted alkyl bromides when Cr^{II}en was used as reductant compared to Cr^{II} (Table 6). In particular, the effect of β -bromine

^{*} Cr^{II}en is expected to be a stronger reducing agent than Cr^{II} due to a larger ligand field stabilization energy induced by ethylenediamine compared to DMF or water ligands. In this respect high spin Cr^{II} (3d⁴) resembles low spin Co¹¹ (3d⁷) with regard to effect of ligands on electron transfer ability.

β-Substituent Y		$\frac{BrCH_2CH_2Y}{+Cr^{tt}en^b}$	$CICH_2CH_2Y$ + $Cr^{11}en^{b}$	CH ₃ CHBrCHYCH ₃ + Cr [™]	
				Erythro	Threo
Bromo	(Br)	25	 	690	310
Trimethylammonium	$[(Me_3)N^+]$	21	28ª	_	
Chloro	(Cl)	5	8 ^{d, e}	26	12
p-Tosyloxy	(TsO)	2	4	4	3
p-Anisoyloxy	$(MeOC_6H_4CO_2)$	1		_	
Acetoxy	(MeCO ₂)	1.0	1.0	1.0	1.0
Hydroxy	(HO)	_		0-3	0.3
Ethyl ^{f,h}	(MeCH ₂)	0-03	-		
Hydrogen	(H)	0.04		0.07	0-07

TABLE 6. RELATIVE RATES OF REDUCTION OF β -substituted alkyl halides by $Cr^{II}en$ and Cr^{IIe}

" In 99.9% v DMF-H₂O solns.

^b At room temp, Cr^{II} (0.0052M) and en (0.022M). Rates determined by competition with trimethylene dibromide by following ethylene and cyclopropane. Relative rates of reduction of ethylene dibromide and trimethylene dibromide = 15.4, ethylene dichloride and trimethylene dibromide = 0.0081. All rates relative to β -acetoxy = 10.

^c Rates from direct measurement, see Ref 23. Approximate relative rates: $BrCH_2CH_2Br + Cr^{11}en$: $ClCH_2CH_2CH + Cr^{11}en$: $BrCH_2CH_2Br + Cr^{11} = 2 \times 10^3 : 1:0.3 at 25^\circ$.

⁴ Rates measured directly by following ethylene formation at 0°; $k_2(\text{Me}_3\text{N}^+) = 2 \cdot 1 \times 10^{-2} \text{ 1/m-sec}$; $k_2(\text{Cl}) = 6.9 \times 10^{-3} \text{ 1/m-sec}$.

* Relative rate determined by competition with trimethylene dibromide is 2.

^f Obtained by competition with ethylene dibromide.

* Ethane was product; all others yield ethylene.

* Butane is the product.

is transmitted more than 10 times as effectively in reactions of β -bromoalkyl halides with uncomplexed Cr^{II} than Cr^{II}en. If we assume that bromine transfer to Cr^{II}en (Eq. 9) is more exothermic than transfer to Cr^{II} (Eq. 8), the transition state for the former should occur earlier along the reaction coordinate than the latter.³² It follows that substituent effects should also be less with Cr^{II}en, in accord with observation.

In each series, a bromine and a trimethylammonium substituent^{*} in the adjacent β -position exerted the largest effects on the rate of reductive elimination. The influence of a β -chlorine was significantly less than bromine. A β -hydroxy substituent as well as its acetyl, anisoyl and tosyl derivatives, had the smallest effects on rate.

The influence of a β -substituent on the rate of reduction of β -substituted alkyl halides by Cr^{II}en or Cr^{II} is not related to its neighboring group effect observed in ionic solvolytic reactions.³³ In the latter category, hydroxy and acyloxy are usually among the most effective, and bromine and the cationic trimethylammonium group among the least capable substituents.

A β -bromine has been shown to assist in homolytic reactions involving addition³⁴ and abstraction.³⁵ It has also been proposed^{18,22} that bromine transfer to Cr^{II}L[†] (Eqs 8 and 9) is assisted by a neighboring bromine via a transition state such as II. The marked acceleration in rates of reduction by a β -trimethylammonium group also leads us to postulate an analogous assistance as in III of similar magnitude.

* Under these conditions, tetraethyl- and tetramethylammonium salts were reduced much slower than β -bromoethyltrimethylammonium ion. Ethane was produced in the former.

† Cr^{II}L is used henceforth to denote chromous species, in general, irrespective of ligands.



Interestingly, an ammonium group per se is not sufficient to cause this rate enhancement. Thus, β -ethylamine in DMF containing 1M perchloric acid was reduced by Cr^{II} much slower ($k_2 < 5 \times 10^{-6}$ l./mole-sec) than either ethylene dibromide or β -bromoethyltrimethyl ammonium bromide under the same conditions ($k_2 = 2.2 \times 10^{-3}$ and 1.6×10^{-4} l./mole-sec,* respectively). No doubt, β -ethylamine under these conditions is completely protonated.† We hope to design further experiments to test the effectiveness of ammonium groups as neighbours which assist homolytic react-tions.‡

The conversion of the intermediate alkyl radical I to alkene by loss of the β -substituent occurs subsequent to the rate-limiting transfer of halogen to chromous (Eqs 8 and 9). This process requires an additional mole of Cr^{II}L, since the overall reaction consumes two moles of Cr^{II}L reagent for each mole of organic halide.

In an earlier paper²² we discussed three competing routes (Y = Br, Eq. 10, 11, 12) by which β -bromoalkyl radicals from vicinal dibromides are converted to alkenes:

$$YCH_2CH_2(I) \to CH_2 = CH_2 + Y \cdot \underbrace{Cr^{II}L}_{Cr^{II}L} Cr^{III}YL$$
(10)

$$\mathbf{I} + \mathbf{Cr}^{\mathbf{I}\mathbf{I}}\mathbf{L} \rightarrow \mathbf{Y}\mathbf{CH}_{2}\mathbf{CH}_{2}\mathbf{Cr}\mathbf{L}^{+2}(\mathbf{IV})$$

$$Y^{-} + CH_2 = CH_2 + Cr^{III}L$$
(11)

$$Cr^{\mu\nu}YL + CH_2 = CH_2$$
(12)

The fragmentation of β -bromoalkyl radicals (Eq. 10) can be obviated by use of excess Cr^{II}L reagent. It is probably not important with such β -substituents as chloro, hydroxy, acetoxy and tosyloxy due to the relatively high heats of formation³⁷ of the corresponding radicals.

Alkenes from β -substituted alkylchromium intermediates. We postulated that an

* Under these conditions, ethylene dibromide reacted with Cr^{II} by the usual second order kinetics observed with other vicinal dihalides. The second order plots for the reduction of β -bromoethyltrimethylammonium ion by Cr^{II} showed upward curvatures indicative of an autocatalytic process. Under these acid conditions the liberated trimethylamine did not appear to be responsible for autocatalysis, since the addition of comparable amounts of trimethylamine to the reduction of ethylene dibromide did not affect the rate of reduction. Chromous amine complexes under these conditions are reversibly formed and the order of addition did not effect the results. The second order rate constant given for β -bromoethyltrimethylammonium ion was determined by initial slopes at several concentrations.

† The rate of reduction of β-bromoethylammonium ion by Cr^{II}en could not be determined since the acid conditions required would deactivate the Cr^{II}en reagent.

 \ddagger Factors involved in determining which groups stabilize an adjacent β -radical center are not completely clear. Part of the participation may be attributable to the stability of the neighboring group as a radical (cf. B. Bohm and P. Abell, *Chem. Revs.* 46, 599 (1962) for a discussion of this point). For example,



In the latter case, ion-radicals such as R₃N[‡] are rather common intermediates of varying stability.³⁶

alkylchromium ion IV is the species²² formed rapidly by reaction of the free radical I with $Cr^{II}L$, and that it is primarily responsible for elimination.²³

The absence of free chloride ion from the reduction of β -chloropropionyl peroxide with Cr^{II} indicates that loss of chloride ion (Eq. 11, Y = Cl) from β -chloroethylchromium ion is not important.* This is also probably true for other substituents such as amino, hydroxy, acyloxy and alkoxy which are generally poorer leaving groups than chloride. By the same process, we reason that β -tosyloxyalkylchromium even more than β -bromoalkylchromium, generates alkenes by loss of tosylate ion (Eq. 11, Y = TsO).

The majority of the substituents examined in this study are eliminated from the alkylchromium intermediate IV synchronously with chromic species as $Cr^{III}Y.$ [†] This includes chloride, hydroxide, carboxylate and amide which are generally poorer leaving groups than bromide and tosylate. The β -bromine substituents is probably unique in participating in all three modes (Eq. 10, 11, 12) of elimination. No doubt the poorer leaving groups require assistance from chromium for elimination and a



transition state such as V is reasonable. In each of these cases, the leaving group Y is characterized by a reasonably available electron pair. Thus, conversion of an amino (β -bromoethylamine) function to an amide or imide (2-bromoethylbenzamide or phthalimide) is sufficient to deactivate the electron pair on nitrogen completely; concerted loss of acylamido Cr^{III} would be unfavored and no reductive elimination obtains. Furthermore, benzamide and phthalimide anions are sufficiently deficient as leaving groups that even loss of these substituents by route (11) is obviated.³⁸ The

$$PhCONHCH_2CH_2Cr^{+2} \xrightarrow{H} PhCONHCH_2CH_3 + Cr^{in}$$
(13)

preferred reaction of β -benzamidoethylchromium is protonolysis (Eq. 13). A similar fate applies to cyano and thionato substituents.

Mechanism of reduction of epoxides by Crllen. Reductive elimination of epoxides

$$CH_2 - CH_2 + 2Cr^{II}en \rightarrow CH_2 = CH_2 + 2Cr^{III}(O^{-2})$$
(14)

by Cr^{II}en can proceed via essentially two routes. It is possible for Cr^{II}L to attack at oxygen or carbon to generate either of two isomeric radicals, VI or VII, respectively.



We associate the much greater reactivity of 2,3-epoxymesityl oxide and styrene oxide compared to cyclohexene oxide to stabilization of the intermediate radical.³⁹ The C-centered radical VI should be much more susceptible to stabilization by a Ph or CO group on the α -C than VII.^{39b} Further reaction with Cr^{II}L would then be analogous to other β -oxyalkylchromium intermediates discussed earlier.

* Due to facile Cr^{II}L catalyzed aquation of Cr^{III}LCl, the quantitative determination of chloride ion in the primary reaction was only possible under conditions in which reduction was rapid.²²

[†] Cr^{III}Y complexes are generally stable to solvolysis under these conditions.³⁸

EXPERIMENTAL

Materials. The following Eastman White label chemicals had the physical properties listed and were used directly: N-2-bromoethylphthalimide, m.p. 83° (lit.⁴⁰: 82-0-83·5°); 3-bromopropionic acid, m.p. 64-65° (lit.⁴⁰ m.p. 62·5°); 3- bromopropionitrile, n_D^{25} 1·4774 (lit.⁴¹ n_D^{25} 1·4789); 2-chloroethanol, n_D^{26} 1·4420 (lit.⁴² n_D^{20} 1·4419); 2-chloroethylacetate, n_D^{26} 1·5326 (lit.⁴³ n_D^{20} 1·4243); 2-chloroethyltosylate, n_D^{26} 1·5326 (lit.⁴⁴ n_D^{20} 1·4243); 2-chloroethyltosylate, n_D^{26} 1·5326 (lit.⁴⁴ n_D^{20} 1·517175 (lit.⁴⁰ n_D^{20} 1·7179); iodobenzene, n_D^{25} 1·6180 (lit.⁴⁰ n_D^{20} 1·619); chlorobenzene, n_D^{25} 1·5225 (lit.⁴⁰ n_D^{20} 1·5248). Eastman 2-bromoethyl acetate was distilled before use, b.p. 75–79°/35 mm, n_D^{28} 1·4534 (lit.⁴⁵ b.p. 67–67·5°/12 mm, n_D^{30} 1·4490).

Aldrich supplied the following materials which were used without further purification: 2-bromoethylphenyl ether, m.p. $32-33^{\circ}$ (lit.⁴⁰ 39°); 2-bromoethylamine hydrobromide, m.p. $172 \cdot 1-172 \cdot 8^{\circ}$ (lit.⁴⁶ 172-173°); 2-bromoethyltrimethylammonium bromide, m.p. 250° d (lit.⁴⁷ 235°); 2-chloroethylamine hydrochloride, m.p. $120-125^{\circ}$ (lit.⁴⁰ 119-123°); cyclohexene oxide, n_D^{25} 1·4514 (lit.⁴⁰ n_D^{20} 1·4519). Aldrich 2-bromoethyl ethyl ether was distilled before use, b.p. $43^{\circ}/19$ mm, n_D^{25} 1·4480 (lit.⁴⁰ b.p. $127 \cdot 8^{\circ}/755$ mm, n_D^{20} 1·447).

Chemicals from K and K Labs were: 2-bromoethanol, n_D^{27} 1:4915 (lit.⁴⁰ n_D^{20} 1:4915); 2-bromoethylchloroformate, n_D^{26} 1:4761; 2-bromoethane sulfonic acid, sodium salt, m.p. 285–290° d; 2-chloroethyl nitrate, n_D^{25} 1:4411.

Columbia Chemicals supplied 2-fluoroethanol, n_D²⁵ 1·3745 (lit.⁴⁰ n_D¹⁸ 1·3647).

1-Bromo-2-chloroethane, n_D^{26} 1.4870 (lit.⁴⁰ n_D^{20} 1.4917) was from Matheson, as was ethylene oxide.

Matheson, Coleman and Bell chemicals were : p-dibromobenzene, m.p. $87-88^{\circ}$ (lit.⁴⁰ m.p., 87°) and bromobenzene, n_D^{25} 1.5575 (lit.⁴⁰ n_D^{20} 1.7598).

From Dow Chemicals were obtained 1,2-dibromoethane, n_D^{26} 1.5353 (lit.⁴⁰ n_D^{20} 1.5389) and ethyleneimine. Vinyl bromide was from City Chemical Corporation and was distilled from the cylinder before use, and β -propiolactone was from Celanese Corporation, $n_D^{32\cdot5}$ 1.4088 (lit.⁴⁰ n_D^{20} 1.4131).

Baker practical grade tris-(2-chloroethyl)-phosphite had n_D^{25} 1.4867 (lit.⁴⁸ n_D^{26} 1.4818) and was used directly, as was 2-chloroethyl methyl ether which had n_D^{25} 1.4867 (lit.⁴⁰ n_D^{20} 1.4111) and which was a gift from Dr. Copelin.

1,2-Dichloroethane was distilled before use, b.p. $82-83^{\circ}$, n_D^{27} 1.4408, (lit.⁴⁰ b.p. $84^{\circ}/760$ mm, n_D^{20} 1.4448). *Preparation of 2-bromoethyl azide*. This material was prepared from 2-hydroxyethyl azide,⁴⁹ n_D^{26} 1.5031. The hydroxyazide was prepared from ethylene oxide and sodium azide.

Preparation of N-2-bromoethylbenzamide. Benzoyl chloride and 2-bromoethylammonium bromide were mixed under Schotten-Baumann conditions.⁵¹ 2-Bromoethylbenzamide was recrystallized twice from benzene, m.p. 106.5-107° (uncorr.); lit. m.p. 105°.

Preparation of 2-bromoethyl-p-toluene sulfonate. p-Toluenesulfonyl chloride (0.1 mole) and 2-bromoethanol (0.1 mole) were added, with stirring, to 100 ml ice cold pyridine. The mixture was stirred at room temp overnight, then acidified with dil HCl and extracted with CCl₄. The product, obtained by evaporation of the solvent, failed to crystallize, even at zero, but its IR spectrum showed no OH bands in the 2.95 μ region, b.p., 164–167°/2 mm; n_{3}^{22} 1.5404.

Preparation of 2-bromoethylphenyl sulfide. This was prepared from sodium thiophenoxide and ethylene dibromide in EtOH, b.p. 98°/1 mm, $n_{\rm D}^{27}$ 1.5574 (lit.⁵² b.p. 134°/23 mm, $n_{\rm D}^{23.53}$ 1.6046).

Preparation of substituted bis(propionyl) peroxides. These were obtained from the corresponding acid chlorides and H_2O_2 .⁵⁴

3-Acetoxypropionyl chloride was prepared from acetyl chloride and β-propiolactone.55

Chromous perchlorate solutions were prepared from chromium metal and perchloric $acid^{20}$ and were 0.5–0.9M in strength.

DMF (Dupont; specified distillation range 0.6°) was used as received. EtOH (Commercial Solvents, gold label, 95%) was purified by distillation from a trace of H₂SO₄ through a 2 ft Oldershaw column, a center cut being used.

Matheson, Coleman and Bell ethylenediamine (98-100%) was used either neat or as a standard soln in DMF.

All operations involving Cr^{II} solns were carried out in a N₂ or He atmo.

General procedure for Cr^{II} en reduction. A soln of 40 ml DMF and 0.5 ml ethylenediamine in a 125 ml flask (capped with a rubber septum) was flushed with He using a hypodermic needle. If O₂ was properly removed from the flask, the addition of 5 ml 0.8N chromous perchlorate soln resulted in a clear blue-purple homogeneous soln. To the magnetically stirred soln was then added 1 ml approximately 0.5M substrate in DMF. The reaction was attended by a change in color from purple to red (or reddish purple) when complete. For qualitative studies, no attempt was made to adjust the ambient temp (25-30°).

When ethylene was the gaseous product, a measured amount of ethane was injected into the reaction vessel. The mixture was stirred vigorously, then a gas sample extracted and analyzed by gas chromatography (internal standard method). Standard mixtures of ethane and ethylene under the same conditions (without substrate) were calibrated on a 6-ft Porapak Q column (Varian Aerograph Co) at 65°. Results were reproducible to within 3%.

Liquid products were analyzed by quenching the mixture with dilute aqueous perchloric acid and extracting with hexane or benzene. The organic extract was dried with Na_2SO_4 and analyzed by gas chromatography.

Kinetics. The rates of reaction between 3-substituted butyl bromides and Cr^{II} were determined by following butene-2 formation. In a typical run a 125 ml flask containing 35 ml DMF was chilled to -15° . To the cooled, well-stirred (magnetic) mixture was added 5.7 ml 7M perchloric acid slowly, and the flask was sealed with a rubber serum cap. The mixture was purged of air with He introduced via a hypodermic needle. An aqueous soln of chromous perchlorate (3 ml; 0.83M) was added to form a clear blue homogeneous soln. Butene-1 (5 ml) was then added as marker gas and the flask placed in the constant temp bath (0°). To commence reaction, a 1 ml aliquot of substrate (0.5M) was added to the equilibrated well-stirred Cr^{II} soln. Gas samples were extracted periodically and analyzed by gas chromatography [15 ft Dowtherm A on firebrick; butene-1 (10 min), *trans*-butene-2 (12.5 min); *cis*-butene-2 (14.4 min)].

Calibration curves for butene-1, *cis*- and *trans*-butene-2 were constructed for various amounts of gases under identical conditions (except substrate). The total amounts of gases removed for gas chromatographic analyses were sufficiently small so that less than 3% overall error was introduced. Rates were reproducible to within 5%, and except in the very slow reactions they were followed to greater than 80%. The rate constants were determined at several concentrations of Cr^{II} and substrate.

Competitive kinetics were performed on the reduction of alkyl bromides with Cr^{II}en reagent, since they were too fast to measure conventionally. Trimethylene dibromide reacted with Cr^{II}en to form cyclopropane quantitatively and was used as the monitoring reaction for reductive elimination of β -substituted ethyl bromides. A large excess (>10-fold) of a predetermined ratio of trimethylene bromide and β -substituted ethyl bromide was added to the Cr^{II}en reagent. The relative amounts of cyclopropane and ethylene were determined by gas chromatography [15 ft Dowtherm A (30%) on firebrick at room temp; ethylene (5·0 min), cyclopropane (7·3 min), n-butane (8·5 min)]. The ratios of trimethylene dibromide and β -substituted ethyl bromides were varied over 10 fold with each alkyl bromide, and the relative rate constants determined in this manner were reproducible to 10% with no apparent trend with concentrations.

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