equation[109] was solved using nonreduced Cox–Antoine vapor pressure data[110] for each liquid at 129 and 131°. The Watson correlations[111] required the critical temperatures of the compounds and their heats of vaporization at the normal boiling points. The former were estimated by the Lydersen method,[112] and the latter calculated using the Fishtine–Kistiakowsky equation.[113] Othmer plots[114,115] for compounds **5, 6, 7, 8,** and **9** were linear, and N-methylacetanilide was used as the reference liquid.[116] The vapor pressure data for the imidates and amides were obtained from a nomograph,[117] and published data were available for the reference liquid.[118] The heat of vaporization of N-methylacetanilide at 130° (14.2 kcal/mol) was calculated using the Clausius–Clapeyron equation as described above; a Watson correlation gave good agreement (14.3 kcal/mol).

The accuracy of the estimation methods in the present applications is unknown, but an uncertainty of ±0.75 kcal/mol for the values in Table X seems reasonable. The agreement among these three sets of values might be misleading because the methods are not strictly independent. The values from the Clausius–Clapeyron calculations were used in the solution of the isothermal energy cycles (Table I).

(109) I. M. Klotz, "Chemical Thermodynamics," W. A. Benjamin, Inc., New York. N. Y., 1964, p 174.
(110) Reference 24a, pp 117–120; the vapor pressures of the liquids at 130°, required for calculation of the standard free energy term limits (Table I), were computed by this method.
(111) K. M. Watson, *Ind. Eng. Chem.*, **35**, 398 (1943).
(112) Reference 24a, pp 8–10.
(113) See ref 24c.
(114) D. F. Othmer, *Ind. Eng. Chem.*, **32**, 841 (1940).
(115) Reference 24b, pp 301, 341, and references cited therein.
(116) The lack of reliable vapor pressure data for **10** precluded the use of the Othmer method for this compound.
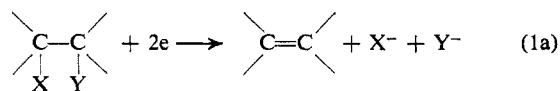
(117) S. B. Lippincott and M. M. Lyman, *Ind. Eng. Chem.*, **38**, 320 (1946).
(118) Reference 24b, p 160.

Stereochemistry of Reductive Elimination by Chromium (II) Complexes

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Abstract: The reductive elimination of *erythro-* and *threo-*2-bromo-3-butyl derivatives of hydroxide, acetate, *p*-tosylate, chloride, and bromide with Cr^{II} was carried out quantitatively under a variety of conditions. With the exception of vicinal dibromides, all of these derivatives gave the same mixture of *cis-* and *trans-*butene-2 from each epimeric pair. In the initial and rate-determining step, an equilibrated free radical is postulated as a common intermediate from each *erythro-* and *threo-*3-substituted butyl bromide by reaction with Cr^{II}. Stereospecificity in reductive elimination of *vicinal* dibromides is attributed to a bromine-bridged radical formed by neighboring group participation in the homolytic removal (ligand transfer) of bromine by Cr^{II}. This is in accord with previous measurements of enhanced rates of reduction of 1,2-dibromides by Cr^{II}. Stereospecific *trans* elimination of vicinal bromines by Cr^{II} can be induced by dimethyl sulfoxide or pyridine as solvent or by the use of excess ethylenediamine as ligand. The bromine-bridged radical is opened stereospecifically by a second Cr^{II} to yield a β-bromoalkylchromium intermediate. Factors which influence *trans* elimination from the latter are discussed. Epoxides also yield alkenes quantitatively with Cr^{II} but the reduction is not stereospecific. Episulfides showed partial stereoselectivity; a more labile sulfur-bridged radical is postulated as an intermediate.

A number of reducing agents are available for reductive elimination of vicinal dihalides to alkenes (eq 1a, X, Y = halogen). Most of these reagents, however,

$$\begin{array}{c} \diagdown \diagup \\ C-C \\ \diagup | \ | \diagdown \\ X \ Y \end{array} + 2e \longrightarrow \begin{array}{c} \diagdown \diagup \\ C=C \\ \diagup \diagdown \end{array} + X^- + Y^- \qquad (1a)$$

are ineffective or react only slowly with the analogous β-substituted alkyl halides (eq 1a, X = halogen; Y = HO, AcO, H$_2$N, etc.). Recently we found that ethylenediaminechrominum(II) reagent is an exceedingly efficient reducing agent, which is particularly effective with organic halides.[1] This versatile reagent will reduce a variety of vicinal dihalides, 2-substituted alkyl halides, and epoxides and episulfides to the corresponding alkene at room temperatures.[2] The reactions afford alkene in high yield and, therefore, offer a potentially useful re-

agent for organic synthesis. As usually conducted, the reaction is homogeneous, and, thus, has certain advantages over those reagents such as zinc in kinetic studies.

Zinc, however, is a useful reagent in dehalogenation of vicinal dibromides, particularly because of the stereospecific *trans* elimination of both bromines in selected cases,[3] especially those derived from simple alkenes.[4,5] In view of versatility of the Cr^{II}en reagent for reductive eliminations, it would be desirable to ascertain the factors which control the stereochemical course of the elimination. In previous studies, we have described our efforts (mostly kinetic) to elucidate the mechanism of

(3) W. Young, Z. Jesaitis, and L. Levanas, *J. Amer. Chem. Soc.*, **59**, 404 (1937); W. Schubert, B. Rabinovitch, N. Carson, and V. Sims, *ibid.*, **74**, 4590 (1952).
(4) House and Ro have cited a number of examples in which debromination with zinc is not stereospecific (H. House and R. Ro, *ibid.*, **80**, 183 (1958).
(5) Recently C. Stevens and J. Valicenti, *ibid.*, **87**, 838 (1965), have demonstrated by use of radiobromine tracers that elimination of bromocyclohexane derivatives by zinc is not stereospecific.

(1) J. Kochi and P. Mocadlo, *J. Amer. Chem. Soc.*, **88**, 4094 (1966).
(2) J. Kochi, D. Singleton, and L. Andrews, *Tetrahedron*, in press.

Table I. Butenes from Reductive Elimination of 2-Bromo-3-butyl Derivatives

2-Bromo-3-Y-butane, Y	Concn, M	Chromous	Concn, M	Temp, °C	Solvent	—Butene-2— trans	cis
meso-Bromo (Br)	0.125 0.0125	Cr^II, H+ a	0.063	0	EtOH^c	73	27
	0.133 0.0133	Cr^II, H+ a	0.063	0	DMF^d	79	21
	0.0121	Cr^II en^b	0.094	25	DMF^e	77	23
	0.0123	Cr^II	0.095	25	DMSO^f	97	3
dl-Bromo (Br)	0.124 0.0124	Cr^II, H+ a	0.063	0	EtOH^c	61	39
	0.150 0.0150	Cr^II, H+ a	0.063	0	DMF^d	48	52
	0.0120	Cr^II en^b	0.094	25	DMF^e	47	53
	0.0122	Cr^II	0.095	25	DMSO^f	8	92
erythro-Chloro (Cl)	0.0131 0.0394	Cr^II, H+ a	0.0565	0	DMF^d	74	26
	0.0128	Cr^II en^b	0.094	25	DMF^e	72	28
	0.0128	Cr^II	0.095	25	DMSO^f	72	28
threo-Chloro (Cl)	0.0126 0.0377	Cr^II, H+ a	0.0565	0	DMF^d	72	28
	0.0123	Cr^II en^b	0.094	25	DMF^e	71	29
	0.0123	Cr^II	0.095	25	DMSO^f	67	33
erythro-p-Tosyloxy (TsO)	0.0514	Cr^II, H+ a	0.0515	0	DMF^d	54	46
	0.00760	Cr^II en^b	0.094	25	DMF^e	54	46
	0.00501	Cr^II	0.095	25	DMSO^f,g	54	46
threo-p-Tosyloxy (TsO)	0.0441	Cr^II, H+ a	0.0515	0	DMF^d	54	46
	0.00962	Cr^II en^b	0.094	25	DMF^e	52	48
	0.00430	Cr^II	0.095	25	DMSO^f,h	54	46
erythro-Acetoxy (CH₃CO₂)	0.0108 0.0310	Cr^II, H+ a	0.0566 0.0542	0	DMF^d	56	44
	0.0106	Cr^II en^b	0.094	25	DMF^e	53	47
	0.0106	Cr^II	0.095	25	DMSO^f,i	52	48
threo-Acetoxy (CH₃CO₂)	0.0104 0.0298	Cr^II, H+ a	0.0566 0.0542	0	DMF^d	57	43
	0.0102	Cr^II en^b	0.094	25	DMF^e	53	47
	0.0102	Cr^II	0.095	25	DMSO^f,i	52	48
erythro-Hydroxy (HO)	0.0115 0.0330	Cr^II, H+ a	0.0566 0.0542	0	DMF^d	51	49
	0.0115 0.0330	Cr^II	0.0566 0.0542	0	DMF^e	50	50
	0.0113	Cr^II en^b	0.094	25	DMF^e	64	36
	0.0113	Cr^II	0.095	25	DMSO^f,k	47	53
threo-Hydroxy (HO)	0.0105 0.0300	Cr^II, H+ a	0.0566 0.0542	0	DMF^d	50	50
	0.0115 0.0330	Cr^II	0.0566 0.0542	0	DMF^e	48	52
	0.0102	Cr^II en^b	0.094	25	DMF^e	63	37
	0.0102	Cr^II	0.095	25	DMSO^f,l	46	54
meso-Chloro (Cl)	0.0131	Cr^II	0.095	25	DMSO^f,m	70	30
dl-Chloro (Cl)	0.0143	Cr^II	0.095	25	DMSO^f,n	70	30

a Perchloric acid (0.90 M). b Ethylenediamine (0.182 M). c 75 vol % ethanol–water. d 90 vol % DMF–water. e 88 vol % DMF–water. f 89 vol % DMSO–water. After 1 hr the reduction was complete to the following extent: g 76%; h 70%; i 85%; j 77%; k 60%; l 52%. After 12 hr the reduction was complete to the following extent: m 97%; n 82%.

these processes;[6,7] in this report we wish to relate the stereochemical consequences of the mechanism. The *erythro* and *threo* pair of 2-halo-3-butyl derivatives were chosen for study because of their accessibility in pure form and the accuracy with which analysis of the products is possible.[8]

Results

Chromous perchlorate was prepared in aqueous solution from chromium metal and dilute perchloric acid.[9]

(6) (a) J. Kochi and D. Davis, *J. Amer. Chem. Soc.*, **86**, 5264 (1964); (b) J. Kochi and D. Buchanan, *ibid.*, **87**, 853 (1965); (c) J. Kochi, *Rec. Chem. Progr.* (Kresge–Hooker Sci. Lib.), **27**, 207 (1966); (d) J. Powers, unpublished studies on the structure and chemistry of alkylchromium species; compare ref 1.

(7) D. Singleton and J. Kochi, *J. Amer. Chem. Soc.*, **89**, 6547 (1967).

(8) We recognize that nonflexibility of a steroidal ring system would provide an even greater degree of requisite rigidity for stereochemical rigor.
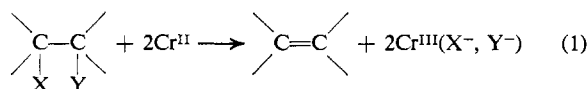
(9) H. Lux and B. Illman, *Ber.*, **91**, 2143 (1958).

Chromous ion is stable in a variety of organic solvents compatible with water. It forms complexes with ligands such as ethylenediamine (en), ethanolamine, and related bases which are soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Ethylenediaminechromium(II) in 90 vol % DMF–water is stable at room temperature for several days in the absence of air. The ethanolamine complexes, on the other hand, will reduce water at a measurable rate under the same conditions.[1]

The reaction of alkyl halide and Cr^II en was carried out in a flask equipped with a gas-tight rubber septum. The solvent was initially purged of air by flushing with helium, and reagents were introduced with hypodermic syringes.

Products. Cr^II en reduced a variety of 2-bromo-3-butyl derivatives to butene-2, quantitatively. The reduction was complete within 15 min at room temperature and was too fast to measure by conventional

techniques. These butyl bromides, however, react with Cr^{II} in the absence of en approximately 10^3–10^4 times slower, and the rates of reduction can be easily followed. The stoichiometry is given by eq 1. The

$$\underset{X\quad Y}{\overset{\diagdown}{C}-\overset{\diagup}{C}} + 2Cr^{II} \longrightarrow \overset{\diagdown}{C}=\overset{\diagup}{C} + 2Cr^{III}(X^-, Y^-) \quad (1)$$

formation of the isomeric cis- and trans-butene-2 was followed by extracting gas samples periodically and analyzing by quantitative gas chromatography (the internal standard method). The reactions were all homogeneous, and it could be shown for a particular bromide that the relative amounts of cis- and trans-butene-2 remained invariant throughout the course of the reaction. Both isomers were, therefore, formed by the same kinetic processes. cis–trans isomerization did not occur under these experimental conditions.

The distributions of cis- and trans-butene-2 obtained from both erythro and threo isomers of 3-substituted 2-butyl bromides under various conditions are given in Table I. These included Cr^{II} in ethanol, dimethylformamide, and dimethyl sulfoxide, as well as Cr^{II}en in DMF. Qualitatively, reactions under these conditions showed wide variations in rates of reduction. With Cr^{II}-en in DMF, even the least reactive 3-substituted 2-butyl bromide was reduced within 15 min at room temperature. The reduction of the same halides by Cr^{II} in DMSO was slightly slower (see footnotes to Table I). Rates of reduction by Cr^{II} in DMF were significantly slower than those carried out in DMSO, but the effect of structure of the halide followed the same reactivity pattern in both solvents (cf. Table I footnotes and Table II). Reduction of vicinal dibromides by Cr^{II} in ethanol

Table II. Rates of Reductive Elimination of 3-Substituted Butyl Bromides with Cr^{II} [a]

3-Y-2-Butyl bromide (Y)	$k_2 \times 10^4$,[d] l. mol^{-1} sec^{-1}		Relative rate[b]	
	erythro	threo	erythro	threo
Hydrogen (H)	0.14	...	0.07	...
Hydroxy (HO)	0.65	0.68	0.3	0.3
Acetoxy (CH_3CO_2)	2.1	2.0	1.0	1
Tosyloxy (p-TsO)	7.7	6.0	4	3
Chloro (Cl)	51	25	25	12
Bromo (Br)	1600	660	780 (390[c])	320 (160[c])

[a] In 85 vol % DMF (H_2O, EtOH) and 0.90 M perchloric acid at 0° (see ref 7). [b] Based on rate for erythro-3-acetoxy-2-bromobutane = 1.0. [c] Corrected for a statistical factor of 2. [d] Product is mixture of cis- and trans-butene-2, except Y = H where product is n-butane.

was slower by a factor of 10^2 than in DMF.[7] In both ethanol and DMF, the less reactive halides were reduced at such a diminished rate that they were not all followed to completion.

There are several features about the results presented in Table I which merit attention. (a) With the exception of meso- and dl-2,3-dibromobutanes, the composition of cis- and trans-butene-2 mixture obtained from each diastereomeric pair of 2-bromo-3-butyl derivatives was the same under equivalent conditions. (b) The ratio of cis- and trans-butene-2 obtained was characteristic of the 2-bromo-3-butyl derivative and depended on the β substituent. (c) Reductive elimination of meso- and

dl-2,3-dibromobutane with Cr^{II} in DMSO solutions afforded high yields of products of trans elimination (i.e., meso → trans-butene-2 and dl → cis-butene-2). (d) The extent of trans elimination of dibromides varied with each diastereomer and depended on the Cr^{II} species as well as solvent. (e) The mixture of cis- and trans-butene-2 obtained from each diastereomeric pair of the other 2-bromo-3-butyl derivatives was largely invariant with Cr^{II} and solvent. The 2-bromo-3-butanol was the exception; Cr^{II}en, which is a reagent used in a basic medium, gave more trans-butene-2.[25]

Effects of Concentration and Temperature on Stereospecificity. In the previous section, the greatest stereospecificity in reductive elimination was shown by meso- and dl-2,3-dibromobutane on reaction with Cr^{II} in DMSO. Furthermore, the dl-dibromide was more dependent on experimental conditions for stereospecific elimination than the meso isomer. The former was thus chosen for further study of the effects of concentration of Cr^{II} and dibromide over a range of temperatures.

In Table III the relative yields of cis- and trans-butene-2 (determined to ±0.2%) from dl-2,3-dibromobutane and Cr^{II} in DMSO are listed. In every case the

Table III. Effects of Concentration and Temperature on Stereospecific Elimination of dl-2,3-Dibromobutane by Cr^{II} in DMSO[a]

dl-2,3-Dibromobutane, M	Cr^{II}, M	Cr^{II}/ $C_4H_8Br_2$	Temp, °C	Butene-2 cis, %	trans, %	cis/ trans
7.1×10^{-3}	2.6×10^{-1}	37	0	95.1	4.9	19.4
7.1×10^{-3}	2.6×10^{-1}	37	20	94.0	6.0	15.7
7.1×10^{-3}	4.4×10^{-2}	6.2	20	93.4	6.6	14.2
7.1×10^{-3}	1.3×10^{-2}	1.8	20	92.8	7.2	12.9
3.9×10^{-3}	1.4×10^{-2}	3.6[b,c]	25	92.6	7.4	12.5
1.3×10^{-2}	1.4×10^{-2}	1.1[b,c]	25	91.6	8.4	10.9
1.3×10^{-1}	1.4×10^{-2}	0.11[b,c]	25	91.0	9.0	10.1
3.9×10^{-1}	1.4×10^{-2}	0.036[b,c]	25	90.5	9.5	9.5
7.1×10^{-3}	4.4×10^{-2}	6.2	51	89.9	10.1	8.9
7.1×10^{-3}	2.6×10^{-1}	37[b]	73	88.0	12.0	7.3
7.1×10^{-3}	2.6×10^{-1}	37[b]	73	88.0	12.0	7.3
7.1×10^{-3}	4.4×10^{-2}	6.2	73	87.8	12.7	7.2
7.1×10^{-3}	4.4×10^{-2}	6.2[b]	73	87.9	12.1	7.3
7.1×10^{-3}	1.3×10^{-2}	1.8	73	87.5	12.5	7.0
7.1×10^{-3}	1.3×10^{-2}	1.8[b]	73	87.6	12.4	7.1
6.3×10^{-2d}	1.3×10^{-2}	0.11	73	86.8	13.2	6.6

[a] In 89 vol % $DMSO$–H_2O solutions. Normal addition, dibromide (0.24 M) added to Cr^{II} with rapid stirring. [b] Inverse addition, Cr^{II} (3 M) added to dibromide. [c] In 97 vol % $DMSO$–H_2O solutions. [d] Added as pure liquid.

over-all yields of butene-2 were quantitative based on the minor reactant. These reductions were rapid even at 10°, but the relative amounts of cis- and trans-butene-2 were not significantly dependent on the order of mixing of the reactants.

Stereospecific formation of cis-butene-2 was dependent on the concentration of Cr^{II} (relative to dibromide) and the temperature. Optimum stereospecificities were obtained at high Cr^{II} concentration and at 0°. However, neither of these effects of Cr^{II} concentration or temperature was pronounced, since at least a 30-fold variation in the former and a 70° temperature range produced less than 10% change in cis-butene-2.

Reductive Elimination of Epoxides and Episulfides. The reductive elimination of cis- and trans-butene-2

Table IV. Reductive Elimination of Epoxides and Episulfides with Cr^{II} Complexes

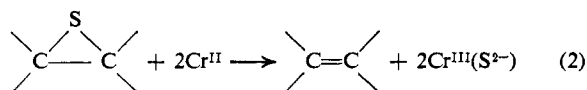| Compound	Concn, M	Chromous	Concn, M	Temp, °C	Solvent	—Butene-2— trans	cis
trans-2-Butene oxide	0.0170	Cr^{II}en[a]	0.092	25	DMF[b]	56	44
		Cr^{II}		25	DMSO[c]	d	
cis-2-Butene oxide	0.0146	Cr^{II}en[a]	0.092	25	DMF[b]	55	45
		Cr^{II}		25	DMSO[c]	d	
trans-2-Butene sulfide	0.0126	Cr^{II}en[a]	0.082	25	DMF[b]	66	34
		Cr^{II}	0.093	25	DMSO[c]	58	42
cis-2-Butene sulfide	0.0137	Cr^{II}en[a]	0.082	25	DMF[b]	28	72
		Cr^{II}	0.083	25	DMSO[c]	20	80

[a] Ethylenediamine (0.178 M).   [b] 86 vol % DMF–H$_2$O.   [c] 87 vol % DMSO–H$_2$O.   [d] Very slow, no product in 3 hr.

Table V. Effect of Solvent on Stereochemistry of Reductive Elimination of 2,3-Dibromobutanes[a]

Dibromide	Concn, M	Cr^{II}, M	Solvent	v/v,[b] %	Dielectric[c] constant	—Butene-2— trans	cis
meso-2,3-Dibromobutane	0.55	0.86	Ethanol	90	24.3	80	20
	0.55	0.86	DMF	90	36.7	82	18
	0.55	0.86	Hexamethylphosphoramide	90	30[d]	79	21
	0.55	0.86	Formamide	90	109[e]	84	16
	0.55	0.86	Sulfolane	90	44	76	24
	0.55	0.86	DMSO	90	45	97	3
	0.55	0.86	DMSO–EtOH (5:10)	90	...	89	11
	0.55	0.86	DMSO–EtOH (1:10)	90	...	81	19
	0.012	0.083	Pyridine	88	12.3	92	8
	0.012	0.083	2,4,6-Collidine–DMF (40:10)	88	f	91	9
dl-2,3-Dibromobutane	0.55	0.86	Ethanol	90	24.3	64	36
	0.55	0.86	DMF	90	36.7	43	57
	0.55	0.86	DMSO	90	45	6	94
	0.017	0.083	Pyridine	88	12.3	18	82
	0.017	0.068	2,4,6-Collidine–DMF (40:10)	88	f	18	82
	0.017	0.068	CH$_3$CN–H$_2$O (30:10)	88	38	53	47

[a] Reactions carried out at 25°.   [b] Vol % solvent, remainder water.   [c] For some empirical parameters on solvent polarity, see A. Parker, *Advan. Phys. Org. Chem.*, **5**, 173 (1967). For an alternative effect of solvents on metal complexes, see oxidation of allylic radicals by Cu^{II} complexes in various solvents [J. Kochi and H. Mains, *J. Org. Chem.*, **30**, 1862 (1965)].   [d] J. Hofmann, A. Schreisheim, and D. Rosenfeld, *J. Amer. Chem. Soc.*, **17**, 2524 (1965).   [e] "Handbook of Physics and Chemistry," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, p E-31.   [f] Reaction was heterogeneous.

epoxides and episulfides were also examined with Cr^{II}-en in DMF and Cr^{II} in DMSO. The epoxides reacted rather slowly with both reducing agents, but produced *cis*- and *trans*-butene-2 quantitatively with the former ($k_2 \simeq 10^{-4}$ l. mol^{-1} sec^{-1} at 25°). The same mixture of butenes was formed from each isomeric epoxide. The episulfides reacted much more readily with both Cr^{II} reagents (Cr^{II}en, $k_2 \simeq 10^{-1}$ l. mol^{-1} sec^{-1} at 25°). The relative amounts of *cis*- and *trans*-butene-2 formed from each isomer varied according to the reactant and the Cr^{II} reagent as shown in Table IV. Thus, partial stereospecificity and *cis* elimination was obtained only

$$\begin{array}{c} S \\ \diagdown \diagup \diagdown \diagup \\ \diagup C——C \diagdown \\ \diagup \qquad \diagdown \end{array} + 2Cr^{II} \longrightarrow \begin{array}{c} \diagdown \qquad \diagup \\ C=C \\ \diagup \qquad \diagdown \end{array} + 2Cr^{III}(S^{2-}) \qquad (2)$$

with the episulfides.

Solvent Effects on Stereospecificity. The stereospecificity shown by the 2,3-dibromobutanes was examined further in other solvents listed in Table V. Pyridine and 2,4,6-collidine also showed stereospecifically enhanced *trans* elimination relative to the other solvents. No correlation is apparent between stereospecificity and bulk properties of the solvent, such as dielectric constant.

Effect of Ligands on Stereospecificity. Since changes in stereospecificity in the reductive elimination of 2,3-dibromobutanes appeared to be largely associated with

changes in coordination around Cr^{II}, other ligands besides ethylenediamine were investigated (Table VI). Large changes in selectivity were achieved by simply increasing the concentration of the ligand, so that an excess of ligand was available for each Cr^{II}. On an equivalent basis, the higher oligomers were more effective than ethylenediamine, but the differences were not sufficiently striking to merit further scrutiny.

Discussion

In a series of *threo*- and *erythro*-2-bromo-3-butyl derivatives which includes hydroxides, acetates, chlorides, bromides, and tosylates, the bromide is alone in showing stereospecificity in reductive elimination with Cr^{II} reagents. Furthermore, the two bromines are removed by *trans* elimination, since the *meso* and *dl* isomers could be made to generate *trans*- and *cis*-butene-2, respectively. Conditions which were optimum for stereospecific *trans* elimination include the use of DMSO or pyridine as solvent or excess ethylenediamine ligand. Lowering the temperature also helped selectivity.
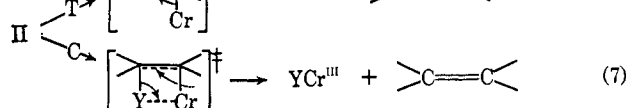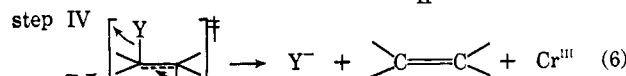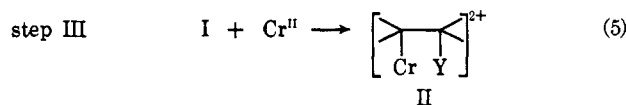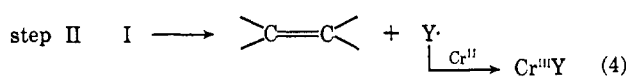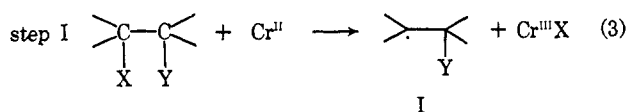
These observations can be readily accommodated by the mechanism previously proposed for reductive elimination.[7,10] In addition, certain features of the intermediates became clearer as a result of these studies.

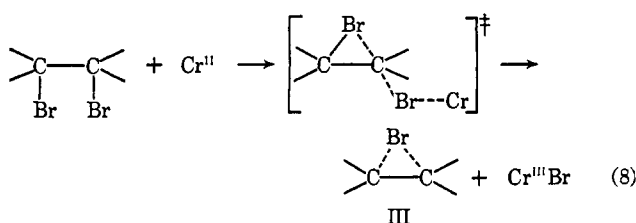The general mechanism for reductive elimination of β-substituted alkyl halides is given by eq 3–7.[6d,7]

(10) W. Kray and C. Castro, *J. Amer. Chem. Soc.*, **86**, 4603 (1964).

Table VI. Effect of Ligands on Stereochemistry of Reductive Elimination

Compound	Concn, M	Cr^{II}, M	Temp, °C	Ligand, M	Solvent, v/v, %	Butene-2 trans	cis
dl-2,3-Dibromobutane	0.0120	0.094	25	Ethylenediamine, 0.18	DMF, 88	47	53
	0.0166	0.083	−15	Ethylenediamine, 0.18	DMF, 86	35	65
	0.0107	0.084	25	Ethylenediamine, 1.63	DMF, 78	22	78
	0.0166	0.083	25	Ethylenediamine, 3.6	DMF, 65	14	86
	0.0166	0.083	25	Ethylenediamine, 7.2	DMF, 44	9	91
	0.0166	0.083	25	Ethylenediamine, 10.8	DMF, 22	8	92
	0.0166	0.083	25	Ethylenediamine, 0.18	DMSO, 86	8	92
	0.0166	0.083	25	Ethylenediamine, 10.8	DMSO, 22	7	93
	0.0166	0.083	25	Ethanolamine, 0.18	DMF, 87	41	59
	0.0166	0.083	25	Ethanolamine, 10.8	DMF, 30	14	86
	0.0166	0.083	25	Trisamino, 0.22	DMF, 72	42	58
	0.0098	0.076	25	Diethylenetriamine, 0.182	DMF, 71	28	72
	0.0107	0.084	25	Triethylenetetramine, 0.086	DMF, 78	47	53
	0.0098	0.076	25	Tetraethylenepentamine, 0.124	DMF, 71	38	62
	0.0098	0.076	25	Pentaethylenehexamine, 0.107	DMF, 71	25	75
meso-2,3-Dibromobutane	0.0120	0.083	25	Ethylenediamine, 10.8	DMF, 22	96	4
	0.0120	0.083	25	Ethanolamine, 10.8	DMF, 22	93	7
	0.0120	0.094	25	Ethylenediamine, 0.18	DMF, 88	77	23

step I $\mathrm{\overset{\displaystyle}{C}{-}\overset{\displaystyle}{C}} + Cr^{II} \longrightarrow \quad I \quad + Cr^{III}X$ (3)

step II $I \longrightarrow\ \mathrm{C{=}C} + Y\cdot \xrightarrow{Cr^{II}} Cr^{III}Y$ (4)

step III $I + Cr^{II} \longrightarrow \left[\mathrm{Cr\ Y}\right]^{2+}$ (II)   (5)

step IV $II \longrightarrow Y^- + \mathrm{C{=}C} + Cr^{III}$ (6)

$\longrightarrow YCr^{III} + \mathrm{C{=}C}$ (7)

Bromine-Bridged Radical as an Intermediate. In order to obtain stereoselectivity in the reductive process, it is necessary that the free radical I does not lose the asymmetry around carbon. This is possible if I exists as a bridged species, since inversion of a trigonal carbon center is generally too rapid to obviate by intermolecular processes. The bridged bromine radical III was postulated previously as an intermediate in reductive eliminations of vicinal dibromides by Cr^{II} as a consequence of the enhanced rate of reduction.[11] This formulation was supported by subsequent studies on the large difference in rates of elimination of cis- and trans-dibromocyclohexanes by Cr^{II}.[7] Step I (eq 3) determines the rate of disappearance of Cr^{II} as well as alkyl halide, since

$$\mathrm{\overset{\displaystyle}{C}{-}\overset{\displaystyle}{C}} \underset{Br\ Br}{} + Cr^{II} \longrightarrow \left[\mathrm{C{-}C} \cdots Br{-}Cr\right]^{\ddagger} \longrightarrow$$

$$\mathrm{C{-}C} \underset{Br}{} + Cr^{III}Br \quad (8)$$

(III)

(11) (a) Kray and Castro[10] were the first to recognize rate acceleration by β-bromine and proposed the bromine-bridged intermediate. (b) A less likely alternative explanation involves a one-step loss of a β-bromine atom synchronously with bromine transfer to Cr^{II}.

the subsequent reaction of free radicals with Cr^{II} (eq 5) is very fast.[12,13] A β-bromine (X, Y = Br) accelerates step I by a factor of 3 × 10^2 compared to a β-acetoxy group (X = Br; Y = AcO). On this scale a β-chlorine increases the rate tenfold and β-tosyloxy by threefold.[7] A β-trimethylammonium group is only slightly less effective than a β-bromine in enhancing reductive elimination. A bridged trimethylammonium ion radical has been proposed as an intermediate.[2] These data are presented in Table II.[7] The same order of reactivity (albeit on a compressed scale) has also been obtained in the reductive elimination of a series of 2-substituted ethyl derivatives with Cr^{II}en.[2]

A bromine-bridged radical such as III was originally formulated by Goering and coworkers to account for stereospecific addition of HBr to bromocyclohexene.[14] Stereochemical studies of homolytic substitution on a variety of alkanes and cycloalkanes by Skell and others have lent convincing support for this formulation.[15]

We postulate that the bridged-bromine radical III has sufficient stability to endure until reaction with Cr^{II} (eq 5).[16] The latter undoubtedly occurs by trans opening (eq 9a) similar to other atom transfer reactions of bromine-[14,15] and iodine-bridged[17] radicals. The carbon–chromium linkage in IIa is sufficiently stable to

(12) We expect reaction of III and Cr^{II} to require almost no activation energy, similar to other reactions of radicals with Cr^{II}.[13]

(13) J. Kochi and P. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965).

(14) H. Goering, P. Abell, and B. Aycock, *J. Amer. Chem. Soc.*, **74**, 3588 (1952). However, these workers subsequently recognized the ambiguity regarding the rationalization of the stereospecific addition of HBr to bromocyclohexene (H. Goering and L. Sims, *ibid.*, **77**, 3467 (1955).

(15) (a) P. Skell and P. Readio, *ibid.*, **86**, 3334 (1964); (b) P. Skell, D. Tuleen, and P. Readio, *ibid.*, **85**, 2850 (1963); (c) Special Publication No. 19, The Chemical Society, London, 1965, p 131; (d) W. Thaler, *J. Amer. Chem. Soc.*, **85**, 2607 (1963); (e) see, however, W. Haag and E. Heiba, *Tetrahedron Letters*, 3683 (1965), for a source of possible complication.

(16) (a) In a similarly constituted system, Goering and Larsen showed that homolytic HBr addition to cis- and trans-2-bromobutene-2 is stereospecific. They primarily employed arguments based on bond rotation in the radical intermediate competing with transfer from HBr. Bromine bridging was also suggested. We find it difficult to accommodate a mechanism based solely on rate of bond rotation vs. reaction with Cr^{II}, because of large differences in selectivities with β substituents. The lifetimes of open β-substituted alkyl radicals in a Cr^{II} environment should not differ so widely from Br, Cl, HO, etc. (b) H. Goering and D. Larsen, *J. Amer. Chem. Soc.*, **81**, 5937 (1959); (c) P. Readio and P. Skell, *J. Org. Chem.*, **31**, 753 (1966); P. Skell and R. Allen, *J. Amer. Chem. Soc.*, **81**, 5385 (1959).

(17) P. Skell and R. Pavlis, *ibid.*, **86**, 2596 (1964).

$$\text{III} + Cr^{II} \longrightarrow \text{IIa} \qquad (9a)$$
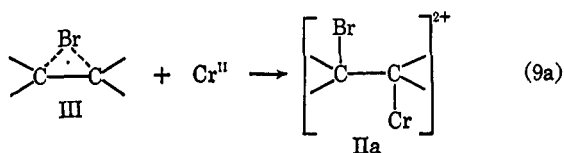
maintain stereochemical integrity until elimination occurs (step IV, eq 6 and 7).[1,18]

The role of a neighboring bromine in affecting the stereochemical course of homolytic reactions has been shown to be dependent on the concentration of the transfer agent. Thus, stereospecificity in homolytic addition of hydrogen bromide to the isomeric 2-bromo-2-butenes[16b] and bromination of optically active 1-bromo-2-methylbutane by molecular bromine[15c] are dependent on the concentration of hydrogen bromide and bromine, respectively. This has been attributed to competition between a first-order transformation of a bromine-bridged radical III to an open radical I (eq 9b) and a second-order reaction of the bridged species with

$$\text{III} \rightleftharpoons \text{I} \qquad (9b)$$
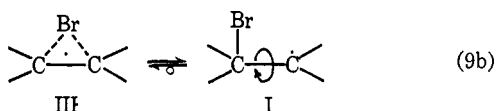
the transfer agent.[15c] As shown in Table III, stereospecificity in reductive elimination of dl-2,3-dibromobutane is dependent in an analogous manner on the concentration of Cr^{II} (eq 9b $vs.$ 9a). The magnitude of the effects of concentration and temperature are roughly comparable in these analogous systems.[19]

Other β substituents which are unable to provide driving force for ligand transfer (eq 3, step I)[6c] by participation yield free radicals I which are unable to maintain their original asymmetry. Further reaction with Cr^{II} produces the same diastereomeric mixture of alkylchromium species II from each of the pair of isomeric reactants (cf. Table I).[20]
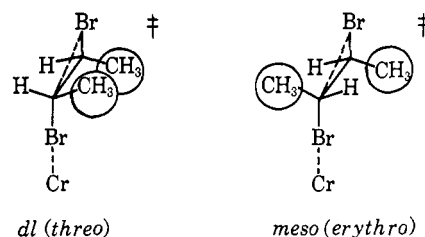
The ease of formation of the bromine-bridged radical differs depending on whether $meso$- or dl-2,3-dibromobutane is the reactant. The over-all stereospecificity obtained under comparable conditions is always better with the $meso$ isomer than the dl isomer (see Tables I, V, and VI). Furthermore, $meso$-2,3-dibromobutane is reduced more than twice as fast by Cr^{II} than the dl isomer (see Table II). These differences can be attributed to the more favorable conformational geometry[21] in the transition state of the former given below.

dl (threo)   meso (erythro)

The faster rate of reduction of the $meso$-2,3-dibromobutane does not appear to be due simply to differences in energies of the reactants since the discrepancy in rates between diastereomers is much less with β-chloro and diminishes entirely with β-hydroxy, acetoxy, and tosyloxy derivatives (see Table II).[21d]

Alkenes from β-Bromoalkylchromium Intermediates by $trans$ Elimination. The stereospecific formation of the β-bromoalkylchromium intermediate IIa[6b] by itself, however, does not ensure complete stereoselectivity. There are two routes by which such metastable species as II afford alkene, and these are designated IVT and IVC (eq 6 and 7, respectively). These paths are distinguishable from each other by examination of products derived from Cr^{II} and Y. $(Cr^{III}Y)^{2+}$ complexes are relatively stable to hydrolysis and can be separated by ion-exchange chromatography from Cr^{III} due to differences in charges on the ions. By examination of bromide and $Cr^{III}Br$ species it has been shown that the β-bromoalkylchromium intermediate IIa (Y = Br) affords alkenes by both paths (IVC and IVT).[7] The relative importance of each depends on the alkyl moiety.
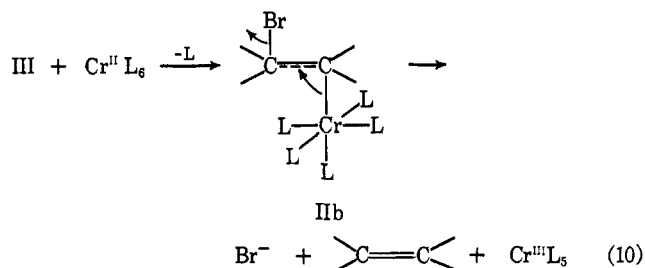
To obtain the stereochemical result reported here, we must postulate that the course of elimination from IIa also be controlled by solvent and ligands coordinated to Cr^{II}. In particular, in order to account for the observed $trans$ elimination from vicinal dibromides we must formulate that alkene formation from IIa occurs via IVT (eq 6) under optimum conditions. The latter include the use of DMSO or pyridine as solvent or excess ethylenediamine as ligand for Cr^{II}. We tentatively postulate that under these conditions water is completely replaced in the coordination sphere of Cr^{II} by DMSO,[22] pyridine, or en. Such a more tightly coordinated chromium species IIb is less likely to be involved in an intramolecular transfer of a β-bromide to form $Cr^{III}L_5Br$ (L = DMSO, py, en) required by path IVC (eq 7).[2] It should, however, be better disposed for $trans$ elimination (eq 6 and 10).[23a]

Other studies have shown that cis elimination of the alkylchromium intermediate II by path IVC (eq 7) re-

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(18) Compare selectivities in reductive cyclization of α,γ-dihalides with Cr^{II}: J. Kochi and D. Singleton, $J. Org. Chem.$, 33, 1027 (1968).

(19) (a) Differences can be attributed to variation in rates of reaction between radicals and various transfer agents. Radicals no doubt react rapidly with HBr[16b] and bromine,[15c] but combination with the paramagnetic Cr^{II} species is probably diffusion controlled.[13] (b) The results of changes in stereochemistry of reductive elimination with Cr^{II} concentration are, however, not unambiguous. Earlier[7] it was shown by examination of products containing Cr^{III} that fragmentation of β-bromoalkyl radicals by ejection of bromine atom (step II, eq 4, Y = Br·) was a competing reaction at low Cr^{II}. The decrease in stereospecificity at low Cr^{II} may be due to such a side reaction and not competition between eq 9a and 9b.

(20) One apparent exception to this is the report by Kray and Castro[10] that slightly different relative amounts of cis- and $trans$-butene-2 were produced from $threo$- and $erythro$-2-iodo-3-chlorobutanes. It is possible to explain this anomaly, however, if one assumes that iodine and chlorine are competitively removed in the initial step. A priori, it is difficult to choose between iodine-assisted removal of chlorine $vs.$ iodine transfer. The former would lead to stereospecificity whereas the latter would not (W. Kray, Jr., private communication.).

(21) (a) Compare the relative population of the $trans$-oriented (bromine) rotamers in $meso$- and dl-2,3-dibromobutanes.[21b,c] (b) A.

Bothner-By and C. Naar-Colin, $J. Amer. Chem. Soc.$, 84, 743 (1962). (c) F. Anet, $ibid.$, 84, 747 (1962). (d) This may not be entirely correct, since vicinal diacetates show greater propensity to exist in $gauche$ conformations than halogens.[21b] (e) Eclipsing effects on conformations in elimination reactions have been discussed: D. Cram, F. Greene, and C. DePuy, $ibid.$, 78, 740 (1956).

(22) (a) D. Holah and J. Fackler, $Inorg. Chem.$, 4, 1721 (1965); (b) Dr. Edward King has kindly informed us that the equilibrium quotients for dimethyl sulfoxide complexes of Cr^{III} are approximately 40 times greater than for aquo ligands. In similar studies, E L. King and D. W. Kemp have shown that ethanol forms weaker complexes than water with Cr^{III} ($J. Amer. Chem. Soc.$, 89, 3433 (1967)); (c) see also K. Ashley, R. Hamm, and R. Magnuson, $Inorg. Chem.$, 6, 413 (1967).

(23) (a) It follows from this mechanism that the products in DMSO should be one bromide and one $Cr^{III}Br$ from each mole of dibromide. Unfortunately, we were unable to determine either Br^- or $Cr^{III}Br$ quantitatively. (b) In a highly constrained system such as cholesterol benzoate dibromide, this mechanism predicts that 1 mol of Br^- should be formed with 1 mol of $Cr^{III}Br$, since only $trans$ elimination is possible from this alkylchromium intermediate.

$$\text{III} + \text{Cr}^{II}\text{L}_6 \xrightarrow{-L}$$

(structure IIb: bromo-alkenyl chromium complex)

IIb

$$\text{Br}^- + {>}\text{C}{=\!=}\text{C}{<} + \text{Cr}^{III}\text{L}_5 \quad (10)$$

quires Y to possess a reasonably available electron pair for coordination to chromium in the transition state.[2] Thus, chloro, hydroxy, acetoxy, alkoxy, and amino as β substituents in reductive eliminations depart as the complex Cr^{III} species (Cr^{III}Y). However, benzamido, phthalimido, and cyano are unable to provide sufficient bonding to chromium. Neither are they good enough as leaving groups to depart anionically *via* route IVT. As a result, the latter yield products of protolytic reduction (eq 11): N-alkylbenzamide and -phthalimide and nitriles, respectively.[2]

$$\text{PhCONHCH}_2\text{CH}_2\text{Cr}^{2+} + \text{H}^+ \longrightarrow \text{PhCONHCH}_2\text{CH}_3 + \text{Cr}^{III}$$
$$(11)$$
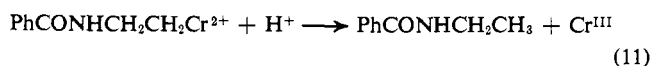
Paths IVC and IVT for elimination of β-bromoalkyl-chromium species are so balanced that slight changes can easily render one more favorable than the other.[23b] We prefer extensive coordination of chromium in II to explain changes in selectivity with changes in solvent, although there are alternative explanations. Thus, DMSO is a particularly useful solvent for dipolar reactions.[24] It is possible that such solvents aid in stabilizing the more polar transition state in IVT than IVC. However, the lack of correlation between stereoselectivity and dielectric constant or ionizing power (Table IV; see footnote c) of the medium indicates that such an effect is not large.

For reductive eliminations of those 2-bromo-3-butyl derivatives which do not proceed stereospecifically, it is difficult at this juncture to account quantitatively for the ratios of *cis*- and *trans*-butenes obtained under various conditions. The loss of asymmetry at the radical stage together with the attendant formation of a mixture of diastereomeric 2-substituted alkylchromium intermediates conspire to render prediction difficult. We see no way of *a priori* determining the composition of this diastereomeric mixture of alkylchromium species.[25] In a number of derivatives, exclusive *cis* elimination (eq 7, Y = Cl, HO, H_2N, etc.) or *trans* elimination (eq 6, Y = TsO) of the alkylchromium species occurs,[2] but this does not necessarily lead to over-all specificity if the radical intermediate is free to epimerize.
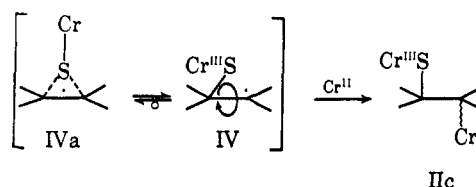
Reductive Elimination of Episulfide–Sulfur Bridging. Epoxides show no stereoselectivity in reductive eliminations by Cr^{II}. In the way of contrast, partial but significant amounts of *trans* elimination are obtained

from *cis*- and *trans*-2-butene sulfides (Table III). We previously presented evidence for the mechanism of reductive elimination of epoxides which favored attack by Cr^{II} on the oxirane function.[2] Oxyalkyl radicals similar to those generated from β-halo alcohols and others were considered intermediates. The latter showed no stereospecificity and, thus, as expected, none was obtained from the former.

The reduction of episulfides probably occurs by an analogous process (eq 12) to generate a β-thioalkyl radical IV. Unlike α-oxy groups, there is considerable

$$\overset{S}{\triangle}{<} + \text{Cr}^{II} \longrightarrow \overset{SCr^{III}}{\underset{}{>}{\cdot}{<}} \quad (12)$$
IV
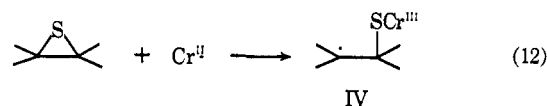
evidence for β-thio bridging in homolytic processes.[26] Such bridging by sulfur does not appear to be as significant as bromine or iodine bridging.[27] The bridged radical IVa is probably formed first in the reduction and then is converted into the open form IV. If IVa[28] is captured by Cr^{II} to yield IIc before conversion

$$\left[\overset{Cr}{\underset{IVa}{\overset{|}{\underset{S}{>}{\cdot}{<}}}} \;\leftrightharpoons\; \overset{Cr^{III}S}{\underset{IV}{>}{\cdot}{<}} \right] \xrightarrow{Cr^{II}} \overset{Cr^{III}S}{\underset{Cr}{>}{\underset{|}{-}}{<}}$$
IIc

to IV, subsequent *trans* elimination of the alkylchromium could lead to stereospecificity.[29] However, the interconversion of bridged and open radicals[30] is probably facile enough to compete with capture by Cr^{II}. This competition can account for the observed lack of *complete* stereospecificity in the removal of sulfur by Cr^{II} species.

The extraction of oxygen and sulfur from epoxides and episulfides by phosphines (and phosphites) is nonspecific (mostly *trans*)[31] in the former and stereospecific (*cis*)[32] in the latter. In these cases, however, the reaction undoubtedly proceeds by nonradical routes. Direct transfer of sulfur to phosphorus has been postulated for reductive elimination of episulfides.
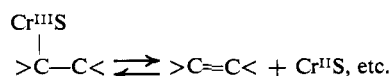
(24) A. Parker, *Quart. Rev.* (London), **1B**, 163 (1962); *Advan. Phys. Org. Chem.*, **5**, 313 (1967); *cf.* also C. Kingsbury, *J. Amer. Chem. Soc.*, **87**, 5409 (1965); R. Alexander, E. Ko, Y. Mac, and A. Parker, *ibid.*, **89**, 3703 (1967); D. Martin, A. Weise, and H. Niclas, *Angew. Chem.*, *Intern. Ed. Engl.*, **6**, 319 (1967); A. Cockerill and W. Saunders, *J. Amer. Chem Soc.*, **89**, 4985 (1967).

(25) Interestingly we observe a small, but significant, increase in *trans*-butene-2 from both *erythro*- and *threo*-2-hydroxy-3-bromobutanes with Cr^{II}en as reducing agent (Table I). Unlike other conditions, these are basic media and the hydroxy group may exist partially as the conjugate base. Intramolecular bonding to chromium could affect the ratio of *threo*- and *erythro*-II.

(26) P. Skell and R. Allen, *J. Amer. Chem. Soc.*, **82**, 1511 (1960); P. Readio and P. Skell, *J. Org. Chem.*, **31**, 759 (1966); H. Szmant and J. Rigau, *Tetrahedron Letters*, 3337 (1967).

(27) B. Bohm and P. Abell, *Chem. Rev.*, **46**, 599 (1962); N. Neureiter and F. Bordwell, *J. Amer. Chem. Soc.*, **82**, 5354 (1960); **79**, 3493 (1957); H. Goering, D. Relyea, and D. Larsen, *ibid.*, **78**, 348 (1956).

(28) It is a moot point whether a radical such as IVa is a Cr^{II} complex with episulfide or a Cr^{III} complex with the thioalkyl radical, If it is stable enough, it may require another Cr^{II} for reduction. In such a case, reduction would be second order in Cr^{II}.

(29) This assumes, of course, that IIc can be induced to eliminate *trans* via IVT (Y = Cr^{III}S) like β-bromoalkylchromium species.

(30) (a) The open radical IV, according to this proposal, is responsible for loss of asymmetry by bond rotation. (b) Alternatively, loss of stereospecificity may be due to loss of sulfur from IV similar to step II in the mechanism, *i.e.*

$$\overset{Cr^{III}S}{\underset{}{>}\text{C}-\text{C}{<}} \;\rightleftharpoons\; {>}\text{C}{=}\text{C}{<} + \text{Cr}^{II}\text{S, etc.}$$

(*cf.* J. Kampmeir, R. Greer, A. Meskin, and R. D'Silva, *J. Amer. Chem. Soc.*, **88**, 1259 (1966), and N. LeBel and A. DeBoer, *ibid.*, **89**, 2785 (1967)).

(31) M. Boskin and D. Denney, *Chem. Anal. Ind.*, 330 (1959).

(32) N. Neureiter and F. Bordwell, *J. Amer. Chem. Soc.*, **81**, 578 (1959).

Experimental Section

Materials. *meso*-2,3-Dibromobutane was prepared from *trans*-butene-2 and bromine in carbon tetrachloride: bp 55.5–56° (22 mm); $n^{25.4}$D 1.5086 (lit.[33] n^{25}D 1.5092, n^{20}D 1.5116). *dl*-2,3-Dibromobutane was prepared from *cis*-butene-2 under the same conditions: bp 63–63.5° (28 mm); $d^{25.4}$D 1.5123 (lit.[33] n^{25}D 1.5125, n^{20}D 1.5143). Gas chromatography showed that each isomer was >99% pure.

meso-2,3-Dichlorobutane was prepared from *trans*-butene-2 and chlorine with antimony pentachloride as catalyst:[34] bp 113°; $n^{25.8}$D 1.4387 (lit.[35] n^{25}D 1.4386). *dl*-2,3-Dichlorobutane was prepared from *cis*-butene-2 in the same manner: bp 117°; $n^{26.2}$D 1.4401 (lit.[35] n^{25}D 1.4409). Both isomers were 100% pure by glpc analysis.

threo-2-Bromo-3-butanol was prepared from *cis*-butene-2 and sodium hypobromite: bp 48–50° (12 mm); n^{26}D 1.4746 (lit.[36] n^{25}D 1.4756). Glpc analysis showed it to be 98% pure. *erythro*-2-Bromo-3-butanol was prepared from *trans*-butene-2 by the same procedure: bp 51–53° (12 mm); n^{26}D 1.4755 (lit.[36] n^{25}D 1.4767). Glpc analysis indicated 97% purity.

erythro-2-Bromo-3-butyl acetate was prepared from the bromohydrin with acetyl chloride in methylene chloride: bp 76–76.5° (20 mm); n^{24}D 1.4496 (lit.[36] n^{25}D 1.4489). Glpc analysis indicated 100% purity. *threo*-2-Bromo-3-butyl acetate was prepared from *threo*-bromohydrin: bp 69–71° (13 mm); n^{24}D 1.4496 (lit.[36] n^{25}D 1.449).

threo-2-Bromo-3-butyl chloride was prepared from *t*-butyl hypobromite, lithium chloride, and *cis*-butene-2 in a ternary mixture of methylene chloride, dimethylformamide, and acetic acid: bp 38–38.5° (16 mm); $n^{24.5}$D 1.4740. Glpc indicated 96% purity (4% dichloride impurity). *erythro*-2-Bromo-3-butyl chloride was prepared from *trans*-butene-2 by the same procedure: bp 31–33° (14 mm); $n^{24.5}$D 1.4740. Glpc analysis showed 94% purity (contaminated with dichloride (2%) and dibromide (4%)).

threo-2-Bromo-3-butyl tosylate was prepared from the *threo*-bromohydrin and tosyl chloride by Tipson's procedure:[37] bp 142–145° (0.05 mm); n^{27}D 1.5312. *erythro*-2-Bromo-3-butyl tosylate was prepared from the *erythro*-bromohydrin using the same procedure: bp 145° (0.05 mm); n^{27}D 1.5305.

cis- and *trans*- butene-2 was obtained from Phillips Petroleum Co., pure grade. Dimethylformamide was obtained from E. I. du Pont de Nemours and Co. as generous samples. Chromous perchlorate was made and used as an aqueous solution (0.8 M).

Ethylenediamine was Matheson Coleman and Bell reagent grade (>99%). Diethylenetriamine was Union Carbide and redistilled, bp 85–100° (4.5 mm). Triethylenetetramine, tetraethylenepentamine, and pentaethylenehexamine were from Dow Chemical Co. and redistilled (bp 135–142° (3 mm), 165–180° (2 mm), and 230–235° (35 mm), respectively) through a <3-ft glass helix packed column. Attempts were made to obtain the most constant-boiling fractions but we are not assured that they were pure (*cf.* brochure from Union Carbide Chemicals Co. (1964): diethylenetriamine, bp 207° (760 mm); triethylenetramine, bp 277° (760 mm); tetraethylenepentamine, bp 340° dec (760 mm)).

trans-Butene-2 oxide was prepared from *erythro*-2-chloro-3-butanol and alkali.[38] The *erythro*-chlorohydrin was prepared from *trans*-butene-2 and calcium hypochlorite. The epoxide had bp 51–54°; n^{32}D 1.3700 (lit.[38] n^{20}D 1.3736). Glpc analysis indicated 94% purity (6% *cis*-epoxide and 2% ethanol from work-up). *cis*-Butene-2 oxide was prepared by the same sequence from *cis*-butene-2 *via* the *threo*-chlorohydrin: bp 59–60°; n^{32}D 1.3761 (lit.[33] n^{20}D 1.3826). Glpc analysis showed 94% purity (6% *cis*-epoxide).

trans-Butene-2 sulfide was prepared from the *trans*-epoxide with thiocyanate:[39] bp 90–91°; n^{27}D 1.4600. Glpc analysis showed absence of the *cis* isomer (lit.[32] n^{20}D 1.4624). *cis*-Butene-2 sulfide was prepared in a similar fashion from *cis*-epoxide: bp 102.5–103°; n^{27}D 1.4746 (lit.[32] n^{20}D 1.4765). Glpc analysis showed greater than 99% purity and no *trans* isomer.

General Procedures for Reductive Elimination. The solvent (DMF, 40 ml) contained in a 125-ml flask capped with a gas-tight rubber septum was flushed with helium (hypodermic needle). All subsequent transfers were made using hypodermic syringes. Aqueous chromous perchlorate (5 ml, 0.855 M) was added and, if oxygen was carefully removed, the resulting solution was clear blue and homogeneous. The purple Cr^{II}en reagent was prepared *in situ* by adding 0.5 ml of ethylenediamine neat or as a solution (in DMF). The β-substituted alkyl halide was added last (0.5 M, 1 ml) and the reduction allowed to proceed at room temperature. For kinetic runs, the reaction vessel was placed in a thermostated water bath. Aliquots of solution were removed and titrated by a procedure described previously.[7]

Analysis. The butene-2 was analyzed by gas chromatography, using the internal standard method. Butene-1 (9.7 min), *trans*-butene-2 (11.8 min), and *cis*-butene-2 (13.6 min) were separated on a Dowtherm A–Firebrick column (25°). A column packed with silver nitrate–diethylene glycol on Firebrick was also used for identification of the gases. Calibration curves were constructed from various amounts and ratios of these three butenes under the same conditions at which the reductions were carried out.

When the reduction was complete a known volume of butene-1 was added as marker and the vessels were vigorously shaken to equilibrate all gases. A small sample of gas was extracted and analyzed by glpc. The same results were obtained if the marker gas was added before the alkyl halide provided the gas samples extracted were small relative to the total volume. Results were reproducible and accurate to within 3%. The relative amounts of *cis*- and *trans*-butene-2 did not suffer from errors inherent in measuring yields by this method and were reproducible to 0.2% or better.

(33) W. Young, R. Dillon, and H. Lucas, *J. Amer. Chem. Soc.*, **51**, 2528 (1929).

(34) M. Hoff, K. Greenlee and C. Boord, *ibid.*, **73**, 3329 (1951).

(35) H. Lucas and C. Gould, *ibid.*, **63**, 2541 (1941).

(36) S. Winstein and H. Lucas, *J. Amer. Chem. Soc.*, **61**, 1580 (1939).

(37) J. Tipson, *J. Org. Chem.*, **9**, 239 (1944).

(38) C. Wilson and H. Lucas, *J. Amer. Chem. Soc.*, **58**, 2396 (1936).

(39) H. Snyder, J. Stewart, and J. Ziegler, *ibid.*, **69**, 2674 (1947).