Kinetic Procedure.—Solutions of *p*-toluenesulfonic acid were used at apparent pH of 1.45 and 1.95. For an apparent pH of 4.5 to 7.0, 2,6-lutidine–*p*-toluenesulfonic acid buffers were used and at apparent pH of 9.4 to 10.8, diisopropylethylamine–*p*-toluenesulfonic acid buffers were employed. The buffered solutions were prepared by diluting aliquots of stock solutions in 50% aqueous dioxane of the appropriate amine and of *p*-toluenesulfonic acid with solvent. Solutions of the desired buffer concentration and apparent pH were obtained by varying the aliquot volumes. Sodium hydroxide solutions were used at an apparent pH of 12.0 and above. Before use, the solutions were cooled in in an ice bath and deoxygenated by bubbling nitrogen through them for 30 min.

Sealed ampoules were employed for reactions run at 100–125°. For reactions at 25.0 and 50.0° glass bottles, which were fitted with silicone rubber seals and screw caps in which a hole had been drilled to allow removal of aliquots with a syringe during the reaction, were used.

Rate constants for the disappearance of ethyl thiobenzoate in 50% aqueous dioxane were calculated from data obtained by measuring the absorbance of the reaction sample at 414 mμ on a Beckman DU spectrophotometer equipped with a photomultiplier. The disappearance of ethyl thionbenzoate was also followed spectrophotometrically at 290 mμ after extraction of reaction samples by the procedure described below. The rate of hydrolysis of ethyl benzoate in 50% aqueous dioxane was determined by extracting reaction samples as described below and analyzing the extracts spectrophotometrically at 230 mμ.

Extraction Procedure.—An 2.016-ml aliquot of the reaction solution was added to a separatory funnel containing 10 ml of cyclohexane and 10 ml of 7% aqueous sodium bicarbonate. When the reaction was carried out in the presence of *p*-toluenesulfonic acid or sodium hydroxide, the aqueous layer was extracted with two additional 5-ml portions of cyclohexane. When an amine buffer was present, the aqueous bicarbonate layer was extracted with one additional 5-ml portion of cyclohexane, the combined extracts were then washed with 10 ml of 5% aqueous hydrochloric acid and the aqueous acid layer extracted with an additional 5-ml portion of cyclohexane. In each case, the combined extracts, *ca.* 20 ml, were diluted to 25 ml for spectrophotometric analysis. Extraction of aliquots of solutions of known ethyl thionbenzoate and ethyl benzoate concentration showed that the recovered amounts of each ester were within ±3% of the original concentration.

Determination of Ethyl Benzoate and Ethyl Thionbenzoate Concentrations During the Reaction.—In order to calculate values of k_2 from eq 4, it is necessary to determine the concentrations of both ethyl benzoate and ethyl thionbenzoate. For runs in the presence of sodium hydroxide, these esters were extracted from the reaction mixture and the absorbance was measured at both 230 and 290 mμ using a Beckman DU spectrophotometer which allows the desired concentrations to be calculated.

For runs at an apparent pH of 1.45 to 10.8, the concentrations of ethyl benzoate and ethyl thionbenzoate were calculated from quantitative gas chromatographic data. Aliquots of the reaction mixture were extracted as described for spectrophotometric analysis except that a known amount of a solution of ethyl phenylacetate in cyclohexane was added to each separatory funnel. The cyclohexane extracts were concentrated at 90–95° to *ca.* 0.5 ml by distilling the solvent through a 6-in. Vigreaux column. Injections of 0.15–0.25 ml samples were made into a 3.5-ft 20% KF-1150 on Chromosorb W column at 120° using an Aerograph A-90 gas chromatograph. The order of appearance of the compounds was ethyl benzoate, ethyl phenylacetate, and ethyl thionbenzoate. Peak areas were measured with a disk chart integrator. The area of the ethyl thionbenzoate peak was corrected for the minor peak in the internal standard by subtracting 0.6% of the area of the ethyl phenylacetate peak.

The calibrations were done by extracting and chromatographing aliquots of solutions of ethyl benzoate and ethyl thionbenzoate of known concentration in 50% aqueous dioxane. Analysis of samples of a solution of known concentrations of ethyl benzoate, ethyl phenylacetate, and ethyl thionbenzoate in cyclohexane before and after treatment with the above extraction procedure indicated that there was no change in relative peak areas within ±2%.

Registry No.—II, 936-61-8; III, 93-89-0; IV, 98-91-9.

Reductive Cyclization of α,ω-Dihalides with Chromium(II) Complexes

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Various 3-substituted alkyl halides are readily reduced by ethylenediaminechromium(II) reagent in DMF solutions at room temperatures. γ-Dihalides and γ-halo tosylates are reductively cyclized in excellent yields to cyclopropanes. Protolytic reduction of the carbon–halogen bond is the most relevant competing reaction. The latter becomes significant when groups in the γ position of alkyl halides are hydroxy, acetoxy, phenoxy, amino, cyano, phthalimido, or triethylammonium. The role of chromous reagent in reductive cyclization is compared with the mechanism of protolytic reduction and the mechanism of reductive elimination of vicinally substituted alkyl halides. Similar free-radical and alkylchromium intermediates are involved in all of these reductive processes. Factors which determine the relative rates of cyclization and protonation of the metastable γ-substituted alkylchromium species are discussed. The effects of γ or β substituents in reductive cyclization or reductive elimination are compared and contrasted; leaving-group ability is considered to be an important attribute for γ substituents in cyclopropane formation. Evidence is presented for neighboring-group participation by a γ-iodine atom in the homolytic removal of the initial halogen by ligand transfer to Cr^{II}en. Stereochemical studies with *meso*- and *dl*-2,4-dibromopentanes show that there is no specificity in cyclopropane formation. Reductive cyclization of α,δ-dihalides and higher homologs with Cr^{II}en was not promising.

Reductive cyclization of α,ω-dihaloalkanes and derivatives is a useful method of preparing cycloalkanes. The stoichiometry of the process (half-reaction) is given by eq 1. Zinc,[1] magnesium,[2] and Grignard reagents[3] have been used as reducing agents. Recently, other novel methods for α,γ cyclization using allyl chloride and diborane[4] as well as azetidine and difluoramine[5] have been reported.

$$XCH_2(CH_2)_nCH_2Y + 2e \longrightarrow \begin{pmatrix} (CH_2)_n \\ CH_2{-}CH_2 \end{pmatrix} + X^- + Y^- \quad (1)$$

(1) R. Shortridge, R. Craig, K. Greenlee, J. Derfer, and C. Boord, *J. Amer. Chem. Soc.*, **70**, 946 (1948); **67**, 1863 (1945); (b) H. Haas, E. McBee, G. Hinds, and E. Glusenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936); M. Murray, *ibid.*, **66**, 812 (1944); J. Battleson, *ibid.*, **68**, 2153 (1946); V. Slabey, *ibid.*, **68**, 1335 (1946); H. Shechter, *Org. Syn.*, **44**, 30 (1964); P. Leriverend and J. Conia, *Bull. Soc. Chim. France*, 116 (1966).

(2) J. Grayson, K. Greenlee, J. Derfer, and C. Boord, *J. Org. Chem.*, **20**, 275 (1955); *J. Amer. Chem. Soc.*, **75**, 3344 (1953).

(3) N. Rabjohn and M. Cohen, *ibid.*, **74**, 6290 (1952); L. Slaugh, *ibid.*, **83**, 2734 (1961); M. Kharasch, M. Weiner, W. Nubenberg, A. Bhattacharya, T. Wang, and N. Yang, *ibid.*, **83**, 3232 (1961); M. Kharasch, J. Sallo, and W. Nudenberg, *J. Org. Chem.*, **18**, 575 (1953); **21**, 129 (1956); C. DePuy, G. Dappen, K. Eilers, and R. Klein, *ibid.*, **29**, 2813 (1964); W. Smith, *ibid.*, **23**, 509 (1958).

(4) N. Hawthorne, *J. Amer. Chem. Soc.*, **82**, 1886 (1960).

(5) C. Bumgardner, K. Martin, and J. Freeman, *ibid.*, **85**, 97 (1963).

Although some attempts have been made to carry our mechanistic studies with the metals, they inherently suffer from lack of solubility. Chromous salts are particularly effective and versatile reducing agents for organic halides.[6] They are readily accessible and solubility in many organic solvents makes them desirable for kinetic studies. The reduction potential of the Cr^{II}–Cr^{III} couple (0.44 V) can be enhanced significantly by complex formation.

The reactivity of organic halides toward Cr^{II}[7] decreases in the order iodide > bromide > chloride and the use of Cr^{II} as a reducing agent has been restricted to the more reactive systems. Recently, we found that the scope of these halide reductions can be increased considerably by use of ethylenediaminechromium(II) reagent,[8] which is simply prepared from Cr^{II} by addition of ethylenediamine. Both of these reagents react by similar mechanisms and differ mainly by the greater reactivity of the latter.

The reduction of the more reactive benzylic and allylic halides, α-halo ketones and analogous compounds by Cr^{II} commonly leads to replacement of halogen by hydrogen (type I, protolytic reduction, eq 2) or dimerization of the alkyl moiety (type II, coupling, eq 3).[9,10] Alkyl and aryl halides, which are too unreactive toward Cr^{II}, require Cr^{II}en for reduction (eq 2).[8]

$$CH_3CH_2CH_2CH_2Br + 2Cr^{II}en + H^+ \longrightarrow CH_3CH_2CH_2CH_3 + 2Cr^{III}en(Br^-) \quad \text{type I} \quad (2)$$

$$2PhCH_2Cl + 2Cr^{II} \longrightarrow (PhCH_2)_2 + 2Cr^{III}(Cl^-) \quad \text{type II} \quad (3)$$

A variety of alkyl halides substituted in the β position react with Cr^{II} and Cr^{II}en, particularly the latter, to afford high yields of alkenes (type III, reductive elimination, eq 4).[11,12] Vicinal dihalides, β-halohydrins, β-haloamines and their derivatives, as well as epoxides and episulfides, are reductively eliminated by these reagents.[13]

$$YCH_2CH_2Br + 2Cr^{II}en \longrightarrow CH_2{=}CH_2 + 2Cr^{III}en(Br^-,Y^-) \quad \text{type III} \quad (4)$$

All three classes of reduction by the Cr^{II} complexes given proceed *via* common intermediates. The reactions follow second-order kinetics, first order in each reactant. Since the activation processes and over-all reactions differ in stoichiometries, multistep sequences are involved. The general steps given by eq 5–9 have been proposed where R_Y denotes an alkyl moiety β substituted with Y. In this mechanism an alkylchromium cation II is common to all three reactions and products are determined by its mode of reaction (eq 7, 8, and 9).

$$R_Y{-}X + Cr^{II} \longrightarrow \underset{\text{I}}{R_Y\cdot} + Cr^{III}X \quad (5)$$

$$\text{I} + Cr^{II} \longrightarrow \underset{\text{II}}{R_YCr^{2+}} \quad (6)$$

$$\text{II} + H^+ \longrightarrow R_YH + Cr^{III} \quad \text{type I} \quad (7)$$

$$\text{II} + R_Y{-}X \longrightarrow (R_Y)_2 + Cr^{III}(X^-) \quad \text{type II} \quad (8)$$

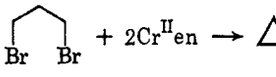
$$\text{II} \longrightarrow R + Cr^{III}(Y^-) \quad \text{type III} \quad (9)$$

In principle, processes 8 and 9 are analogous since a carbon–carbon bond in each is constituted from reaction of a carbon–chromium and a carbon–halogen bond (Y = halogen) by intermolecular and intramolecular processes, respectively. By extending this argument, it should be possible to cyclize a γ-substituted alkyl halide to cyclopropanes and higher homologs to larger cycloalkanes. In this report we wish to describe our studies directed toward exploring the mechanisms of such cyclizations.

Results and Discussion

Chromous perchlorate solutions were prepared from pure chromium by dissolution in 1 *M* aqueous perchloric acid.[14] All reactions were carried out in 90 vol % dimethylformamide (DMF)–water in the absence of air. Rubber serum capped flasks with solvent were flushed with nitrogen and an aliquot of Cr^{II} solution was added *via* a hypodermic syringe. Addition of a measured amount of ethylenediamine (en) to the clear blue chromous perchlorate solution generated Cr^{II}en[15] (purple) *in situ*. Organic halide was added finally and the homogeneous mixture was allowed to react at room temperature.

A series of trimethylene halides listed in Table I was treated with Cr^{II}en under these conditions. Trimethylene diiodide and dibromide reacted completely with Cr^{II}en within 10 min and afforded quantitative yields of



$$+ 2Cr^{II}en \longrightarrow \triangle + 2Cr^{III}en(Br^-) \quad (10)$$

cyclopropane. On the other hand, trimethylene dichloride as well as the iodochloride and bromochloride reacted with excess Cr^{II}en to afford to a mixture of cyclopropane and propane, quantitatively. The same mixture of hydrocarbons (Table I) was obtained irrespective of the trimethylene chlorohalide employed. The pro-

TABLE I

REDUCTIVE CYCLIZATION OF TRIMETHYLENE DIHALIDES WITH Cr^{II}en[a]

$XCH_2CH_2CH_2Y$						Distribution	
X	Y	Concn, *M*	Cr^{II}, *M*	en, *M*	Conversion, %	Propane	Cyclopropane
I	I	0.013	0.09	0.18	94	<0.02	100
Br	Br	0.014	0.09	0.18	98	<0.05	100
I	Cl	0.018	0.09	0.18	94	18	82
I	Cl	0.018	0.09	1.8	100	<0.05	100
Br	Cl	0.019	0.09	0.18	98	19	81
Br	Cl	0.019	0.09	1.8	100	<0.05	100
Cl	Cl	0.013	0.09	0.18	100	14	86
$XCH(CH_3)CH_2CH_2Y$						*n*-Butane	Methylcyclopropane
Br	Br	0.016	0.09	0.18	100	6	94
Br	Br	0.016	0.09	11	100	4	96
Cl	Cl	0.024	0.09	0.18	...	24	76
Cl	Cl	0.024	0.09	11	95	1	99

[a] Substrate added (by syringe) to excess Cr^{II}en reagent in 10 vol % aqueous DMF at room temperature.

(6) J. Kochi, *Rec. Chem. Progr.*, **27**, 207 (1966).

(7) Cr^{II} is used to denote chromous ion in aqueous solutions of DMF and other solvents. Hexacoordination with solvent is indicated, but no attempt will be made to specify coordination unless necessary for the discussion.

(8) J. Kochi and P. Mocadlo, *J. Amer. Chem. Soc.*, **88**, 4094 (1966).

(9) J. Kochi and D. Davis, *ibid.*, **86**, 5264 (1964).

(10) J. Kochi and D. Buchanan, *ibid.*, **87**, 853 (1965).

(11) W. Kray and C. Castro, *ibid.*, **86**, 4603 (1964).

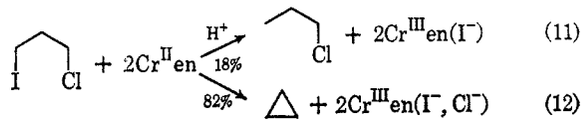
(12) D. Singleton and J. Kochi, *ibid.*, **89**, 6547 (1967).

(13) J. Kochi, D. Singleton, and L. Andrews, *Tetrahedron*, in press.

(14) H. Lux and G. Illman, *Ber.*, **91**, 2143 (1958).

(15) Cr^{II}en denotes the ethylenediaminechromium(II) reagent obtained by reacting Cr^{II} and ethylenediamine in a 1 to 2–3 *M* ratio. It consists largely of the bisethylenediaminechromium(II) complex. *Cf.* R. Pecsok and J. Bjerrum, *Acta. Chem. Scand.*, **11**, 1418 (1957).

pane arose by the stepwise protolytic reduction of trimethylene iodochloride (0.73 mmol), since only cyclopropane (0.59 mmol, 81%) and *n*-propyl chloride (0.12 mmol, 16%) were formed when the reaction was quenched with oxygen after 5 min. Independently, it was shown that Cr^{II}en reagent converted *n*-propyl chloride much more slowly than *n*-propyl iodide into propane.



(11)

(12)

The competition between reductive cyclization and protolytic reduction also occurred in 1,3-dihalobutanes as shown in Table I. In this system, protolytic reduction was relatively more important than it was in the corresponding trimethylene dihalide.

The rate of the reaction between trimethylene dihalides and Cr^{II}en was first order each in Cr^{II}en reagent and dihalide. The second-order rate constant for trimethylene dibromide and Cr^{II}en at 0° in 10 vol % aqueous DMF was 0.36 l./mol sec.

In this regard, the kinetics of the cyclization were similar to protolytic reductions of organic monohalides (eq 2)[8,16] and reductive elimination of vicinal dihalides (eq 4).[11-13] Likewise, a multistep sequence and formation of metastable intermediate(s) are indicated for cyclization. Under similar experimental conditions the relative rates of reduction of *n*-butyl iodide, bromide, and chloride decreased in this order: 7×10^3, 5×10^2, 1, respectively.[16] In view of these large differences in rates of halogen transfer, we conclude that reaction between trimethylene iodochloride or bromochloride and Cr^{II}en occurred initially at the iodine and bromine sites. Thus, the same intermediate was generated from trimethylene iodochloride, bromochloride, and dichloride. Partitioning of this intermediate to cyclopropane and *n*-propyl chloride must have occurred subsequent to transfer of the first halogen to Cr^{II}en.

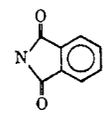
The formation of cyclopropane quantitatively from trimethylene diiodide and dibromide indicated that the analogous intermediates from these compounds generate only cyclopropane. The effect of various γ substituents on cyclopropane formation in a series of 3-substituted propyl halides is given in Table II.

Reductive Cyclization and Elimination *vs.* Protolytic Reduction.—In reductive elimination and cyclization of 2- and 3-substituted alkyl halides by Cr^{II}en, the principal competing reaction was protolytic reduction (eq 2). The latter proved to be a useful measure of the ease with which various substituents in the β and γ positions were removed. Factors which affect the loss of a β substituent and a γ substituent in the two series are not precisely the same. A γ-halogen substituent was not required since γ-tosyloxypropyl bromide and chloride also reacted with Cr^{II}en to produce cyclopropane quantitatively. The analogous γ-hydroxy-, acetoxy-, and aminopropyl halides, on the other hand, gave no cyclopropane, but yielded only the product of protolytic reduction, *i.e.*, propyl alcohol, acetate, and amine, respectively.

(16) J. Powers, unpublished observations. The structure and chemistry of alkylchromium species will be presented later.

TABLE II

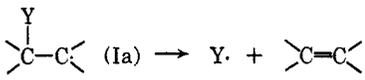
REDUCTION OF 3-HALOPROPYL DERIVATIVES WITH Cr^{II}en[a]

—XCH₂CH₂CH₂Y— X	Y	Concn, *M*	—Conversion, %— Propane	Cyclopropane	Product
Br	OH	0.015	<0.02	<1	Propyl alcohol
Br	OTs	0.010	<0.02	100	...
Br	OAc	0.015	<0.05	<0.1[b]	Propyl acetate
Br	CN	0.010	<0.05	<1	Butyronitrile
Br	$N^+(C_2H_5)_3$	0.010	<0.02	<1	Triethylpropylammonium
Br	NH_2	0.010	<0.05	<0.1	Propylamine
Br		0.016	<0.02	<0.1	N-Propylphthalimide
Br	OPh	0.30	<0.03	<0.1	Propyl phenyl ether
Cl	OH	0.022	<0.02	<0.1	Propyl alcohol
Cl	OTs	0.024	<0.05	95	...

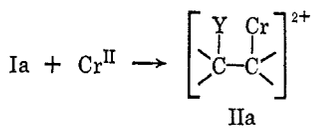
[a] Substrate added to excess Cr^{II}en reagent in 10 vol % aqueous DMF at room temperature. Cr^{II} (0.09 *M*) and ethylenediamine (0.18 *M*). [b] Quantitative yields of *n*-propyl acetate formed.

In 1,2 eliminations, β-hydroxy-, β-phenoxy-, β-acetoxy-, and β-aminoethyl bromides and chlorides afforded only ethylene and no protolytic reduction. Phthalimido and cyano substituents in neither β-ethyl nor γ-propyl halides were eliminated in reactions with Cr^{II}en, since N-ethyl- and N-propylphthalimides as well as propionitrile and butyronitrile were reduction products from the corresponding bromides and chlorides.

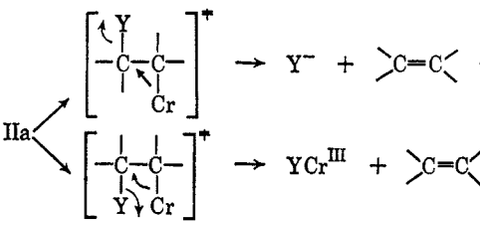
Mechanism of Cyclopropane Formation.—Reductive elimination of β-substituted alkyl halides with $Cr^{II}L$[17] had been postulated to proceed *via* a β-substituted alkyl radical I (eq 4, R_Y = β-Y-alkyl). Alkene is formed *via* three competing processes (eq 13, 14, and 15).[12] The β fragmentation (eq 13) is only important



(13)



IIa



(14)

(15)

Y = I, Br

with β-bromo and iodo substituents and it can be obviated by use of excess $Cr^{II}L$ reagent. In the latter case, reaction between $Cr^{II}L$ and radical Ia is sufficiently fast such that subsequent elimination only occurs from the alkylchromium intermediate IIa.[16] The relative importance of routes 14 and 15 in elimination is largely dependent on the nature of Y. For tosyloxy, the displacement of tosylate ion (eq 14) was preferred, whereas no chloride ion was formed from β-chloroethyl-

(17) $Cr^{II}L$ is used generically to denote all chromous species, irrespective of ligands.

chromium ion and elimination generated only $ClCr^{III}$ (eq 15). A β-bromoalkylchromium intermediate produced alkene by both paths concurrently. Tosylate and to a certain extent bromide are favored leaving groups in nucleophilic displacements[18] and unimolecular solvolyses.[19] Other substituents such as chloride, acetate, hydroxide, or amide are poorer leaving groups. The distinction between these paths for fragmentation of II lies primarily in the ability of the leaving groups to depart as anions (eq 14). The alternative path requires synchronous bonding to chromium to facilitate departure (eq 15) of those β substituents which are poorer leaving groups. A transoid transition state has been postulated for the former and a cisoid one for the latter.[12] Acylamido, phthalimido, and cyano groups are sufficiently poor in both capacities so that protonolysis (eq 7) is more favorable than either route for elimination.

Kinetic studies support a similar mechanism for reduction of 3-substituted alkyl halides. The intermediate propyl radical III is formed by halogen transfer to $Cr^{II}en$ (eq 16). In contrast to the behavior of β-

$$YCH_2CH_2CH_2Br + Cr^{II}en \longrightarrow YCH_2CH_2CH_2\cdot + Cr^{III}X \quad (16)$$

iodo- or β-bromoalkyl radicals, fragmentation of γ-iodo- or γ-bromopropyl radicals to cyclopropane does not appear to be a spontaneous process at these temperatures.[20] Reaction of III with Cr^{II} leads to a γ-substituted propylchromium intermediate IV similar to the β-substituted analogs II from 1,2-dihalides.

$$\text{III} \nrightarrow \triangle + Y\cdot \quad (17)$$

$$\text{III} + Cr^{II}en \longrightarrow \underset{\text{IV}}{YCH_2CH_2CH_2Cren^{2+}} \quad (18)$$

Y = I, Br

The alkyl chromium intermediates II and IV show different abilities to undergo 1,2 and 1,3 eliminations, respectively. Thus, groups such as hydroxy, phenoxy, acetoxy, alkoxy, and amino which require coordination to chromium in 1,2 eliminations are not removed at all in 1,3 systems. Quantitative yields of cyclopropane are obtained from propylchromium derivatives IV only with γ substituents such as iodo, bromo, and tosyloxy, which are favored leaving groups in anionic displacements, and which can also depart unassisted from β-substituted analogs II (eq 14). Furthermore, in γ-chloropropylchromium, cyclization (eq 20) and protonolysis (eq 19) are so balanced that the former is only four times faster than the latter. However,

$$ClCH_2CH_2CH_2Cren^{2+} \xrightarrow{H^+} ClCH_2CH_2CH_3 + Cr^{III}en \quad (19)$$

$$ClCH_2CH_2CH_2Cren^{2+} \longrightarrow Cl^- + \triangle + Cr^{III}en \quad (20)$$

protonolysis of alkylchromium species in aqueous DMF is retarded by bases.[16] The competition between cyclization and protonolysis of γ-chloropropyl chromium can be altered to favor the former simply by use of excess en to act as a base. Thus, γ-chloropropyl iodide, bromide, and chloride react with $Cr^{II}en$ in the presence of excess en (see Table I) to afford quantitative yields of cyclopropane.

In Table III a variety of γ substituents are listed together with the mode of decomposition of the corresponding propylchromium derivative and L, the leaving group constant. The latter is obtained from the equation $\log (k_i/k_0) = \gamma L$, which correlates the rates of nucleophilic substitution of a series of alkyl derivatives.[18] A similar parameter can be obtained from solvolysis reactions. For comparison, values are also given in Table III for the formation of ethylene by reductive elimination of the lower homologs, 2-substituted ethyl halides, with the same $Cr^{II}en$ reagent. We postulate that cyclopropanes are only formed from γ-substituted propylchromium intermediates IV by an internal displacement process (eq 21), which is similar to eq 14 in β eliminations. The alternative decomposition of IV by loss of YCr^{III} in a cyclic transition state (eq 22) similar to a *cis* elimination (eq 15) in 1,2 systems does not appear relevant (*vide infra*).

TABLE III

COMPETITION BETWEEN CYCLIZATION, ELIMINATION, AND PROTONOLYSIS IN REACTIONS OF γ- AND γ-SUBSTITUTED ALKYLCHROMIUM DERIVATIVES

Substituent Y		γ-Y-Propylchromium[a]	β-Y-Ethylchromium[b]	Leaving-group constant[c] L
p-Tosyloxy	(TsO)	Δ	=	0.63
Bromo	(Br)	Δ	=	0.00
Iodo	(I)	Δ	=	0.04
Chloro	(Cl)	Δ + H	=	−1.61
Trimethylammonium	[$(CH_3)_3N^+$]	H	=	−3.54
Acetoxy	(CH_3CO_2)	H	=	−4.68
Methoxy	(CH_3O)	H	=	<−6.54
Hydroxy	(HO)	H	=	*d*
Benzamido	(PhCONH)	H	H	*d*
Cyano	(NC)	H	H	*d*
Amino	(H_2N)	H	=	*d*

[a] Δ denotes cyclization, H denotes protonolysis. [b] = denotes elimination. [c] From ref 18. [d] Where L has not been determined, relative order is assumed.

$$\text{IV} \rightarrow \left[\begin{array}{c} Y \\ \diagdown \\ Cr \end{array}\right]^{\ddagger} \longrightarrow Y^- + \triangle + Cr^{III} \quad (21)$$

$$\text{IV} \rightarrow \left[\begin{array}{c} \diagup Y \\ Cr \end{array}\right]^{\ddagger} \longrightarrow \triangle + YCr^{III} \quad (22)$$

Anionic character is not highly developed in the transition state of the cyclization (eq 21), since the driving force for internal displacement of the γ substituent is not large. Only readily displaced groups such as iodide, bromide, and tosylate and to a certain extent chloride are ejected. Acetate, phenoxide, and trimethylamine, which are undistinguished as leaving groups go, are not displaced and the intermediate IV is preferentially protonated. Furthermore, $Cr^{II}en$ undoubtedly reacts with 1,3-dihalobutanes (Table I) *via* transfer of the secondary rather than the primary

(18) E. Thornton, "Solvolysis Mechanisms," Ronald Press, Inc., New York, N. Y., 1964, p 163 ff.

(19) A Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 82.

(20) There are differing indications concerning the cyclization of γ-iodopropyl radicals to cyclopropane (*cf.* D. Blomstrom, K. Herbig, and H. Simmons, *J. Org. Chem.*, **30**, 959 (1965); L. Kaplan, *J. Amer. Chem. Soc.*, **89**, 1753, 4566 (1967)). In both cases, much elevated temperatures were employed compared to studies reported here.

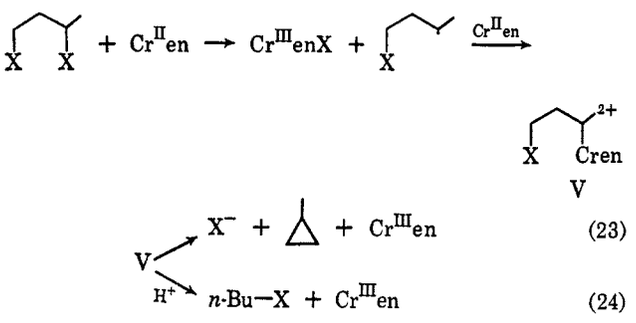
TABLE IV

RELATIVE RATES OF REDUCTION OF ORGANIC HALIDES WITH $Cr^{II}en$ BY COMPETITION STUDIES[a]

Substrate A	Coreductant B	k_A/k_B	Relative rates A
$CH_3CH_2CH_2CH_2Br$	$BrCH_2CH_2CH_2Br$	0.015 ± 0.002	0.015
$(CH_3CH_2)_3N^+CH_2CH_2CH_2Br$	*b*	...	~0.3[c]
$CH_3CH_2CH_2CH_2I$	$ICH_2CH_2CH_2I$	0.017 ± 0.003	0.43
$ClCH_2CH_2CH_2Br$	$CH_3CH_2CH_2CH_2Br$	14 ± 2	0.22
$TsOCH_2CH_2CH_2Br$	$CH_3CH_2CH_2CH_2I$	1.1 ± 0.1	0.47
$ClCH_2CH_2CH_2I$	$CH_3CH_2CH_2CH_2I$	6 ± 0.5	2.7
$BrCH_2CH_2CH_2Br$	$BrCH_2CH_2Br$	0.065 ± 0.001	1.0
$ICH_2CH_2CH_2I$	$BrCH_2CH_2Br$	1.6 ± 0.2	25

[a] Cr^{II} added rapidly (by syringe) to solutions of excess halide mixture, ethylenediamine in DMF at room temperature. All solutions homogeneous and $Cr(ClO_4)_2$ was 0.0052 *M* and ethylenediamine was 0.020 *M*. For substrate concentrations see Table VI, Experimental Section. [b] Determined by following Cr^{II} disappearance. Second-order plot curved upward slightly; $k_2 = 7.7 \pm 1.6 \times 10^{-5}$ l./mole sec. In solutions of 20% aqueous DMF containing 1 *M* perchloric acid $Cr^{II}_0 = 0.037$ *M*, bromoammonium salt = 0.010 *M*. Under the same conditions trimethylene dibromide, $k_2 = 2.7 \times 10^{-4}$ l./mole sec. [c] Relative rate estimated from *b* by assuming the same relative reactivity for Cr^{II} and $Cr^{II}en$. Therefore, value is lower limit.

halogen, owing to the greater reactivity of the former. The attendant secondary alkylchromium intermediate V is less inclined to eject the γ-halide (eq 23) than the



primary analog IV and protonolysis (eq 24) is a more important competing process. This behavior is in accord with the stability of alkylchromium species, which generally increase in the order primary < secondary < tertiary.[8,16]

Grignard reagents substituted in the γ position even with such poorer leaving groups as alkoxides afford cyclopropanes in good yields.[2,3] These organomagnesium compounds undoubtedly evoke more carbanionic character, as does the recently reported electrochemical reduction of 3-substituted propyl halides.[21]

Participation in Halogen Transfer to Cr^{II}.—In addition to affecting products of reduction, γ substituents also alter the rate of loss of halogen to Cr^{II} (eq 5). The rates of disappearance of Cr^{II} and alkyl halide in these reductions are directly related to this step, since the subsequent association of radicals (eq 6) with another Cr^{II} is fast. The relative rates of reduction of various halides in Table IV with $Cr^{II}en$ were measured by a competitive method since reactions were too rapid to follow by conventional techniques.

In Table V, the relative rates of reduction of γ-substituted propyl halides by $Cr^{II}en$ are compared to the parent propyl halide. The corresponding data for relative rates of reductive elimination of a series of β-substituted ethyl bromides[13] are also included for comparison. We further conclude from the data presented in Table V that the γ-iodo substituent increases the rate of halogen transfer to $Cr^{II}en$. A similar effect is even more evident with a β-bromo substituent in 1,2 eliminations (column 4). The effect of a β-iodo substituent could not be examined owing to instability of 1,2-diiodides.[22]

TABLE V

RELATIVE RATES OF REDUCTION OF γ-SUBSTITUTED PROPYL HALIDES BY $Cr^{II}en$[a]

		Relative rates[b]		
Substituent Y		γ-Y-Propyl iodide	γ-Y-Propyl bromide	β-Y-Ethyl bromide[c]
Methyl	(CH_3)	1	1	1
Chloro	(Cl)	7	20	100
p-Tosyloxy	(TsO)	...	30	60
Bromo	(Br)	(10)[d]	70, 35[e]	600, 300[e]
Iodo	(I)	60, 30[e]	(100)[f]	...

[a] In aqueous DMF solutions at room temperature. [b] Relative rates given only to one significant figure for emphasis. [c] See ref 13. [d] Estimate by interpolation. [e] Statistical correction of two applied. [f] Estimate by extrapolation. See text.

The effect of a γ-iodine in accelerating the rates of reductive cyclization of 1,3-dihalides merits further discussion. These rates can be compared by using the least reactive halogen, *i.e.*, a γ-chlorine, as a standard for comparison. Thus, as shown in Table V, in the series of propyl iodides a γ-iodine is four to five times more effective than a γ-chlorine. In a corresponding series of propyl bromides, the γ-bromine increases the rate of reduction less than twice as much as a γ-chlorine. The greater effectiveness of a γ-iodo substituent compared to a γ-bromine given by these *parallel* studies is certainly a lower estimate, since *n*-butyl iodide is approximately 30 times more reactive than *n*-butyl bromide toward $Cr^{II}en$ (Table IV). As a result, substituent effects in the more reactive iodide series are transmitted less than they are in the bromide series,[23a] as shown further by the sevenfold acceleration by γ-chlorine in the iodide series and a 20-fold effect effect felt in the bromide series. Unfortunately, the study of 3-bromo-1-iodopropane is not meaningful owing to the ambiguity regarding which halogen is initially transferred to $Cr^{II}en$ (*i.e.*, iodine transfer or iodine-assisted bromine transfer). We anticipate, however,

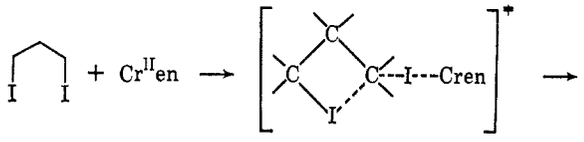
(21) M. Rifi, *J. Amer. Chem. Soc.*, **89**, 4442 (1967).

(22) F. Jensen and W. Coleman, *J. Org. Chem.*, **23**, 869 (1958); M. Cava and D. Napier, *J. Amer. Chem. Soc.*, **79**, 1701 (1957); T. Paterson and J. Robertson, *J. Chem. Soc.*, **125**, 526 (1924).

(23) (a) This also follows from Hammond's postulate (G. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955)). The compressed reactivity scale also applies to reactions of Cr^{II} and $Cr^{II}en$ (see ref 13). (b) These rough estimates are obtained by a simple extrapolation and interpolation of the data presented in Table V. (c) We have no evidence which indicates that γ-iodopropyl radical, as the bridged cyc  lic species has sufficient stability to be treated in its *subsequent* reactions separately from the open chain form. Evidence for bridged β-iodoalkyl radicals has been presented (P. Skell and R. Pavlis, *ibid.*, **86**, 2956 (1964)).

that a γ-iodine would assist *bromine transfer* to Cr^{II}en by a factor of greater than 100 compared with a tenfold acceleration of *iodine transfer* by γ-bromine.[23b] These substituent effects would be even further magnified if Cr^{II} were used as the reductant rather than Cr^{II}en.[13]

We attribute the accelerating effect of a γ-iodo substituent on the rate of reduction to its neighboring-group participation during halogen transfer to Cr^{II}-en.[24] A transition state for this assistance is given in eq 25.[23c] A similar participation by iodine has been



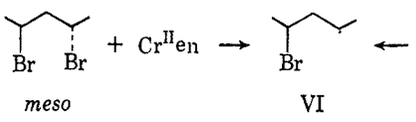
$$Cr^{III}Ien + ICH_2CH_2CH_2\cdot \quad (25)$$

proposed in the thermolysis of aroyl and acyl peroxides.[25a] In those cases, however, a five- rather than a four-membered transition state would be invoked.[25b]

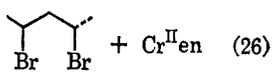
Neighboring-group participation by β-bromine in reduction of alkyl halides by Cr^{II} was shown both to affect the rate[12] strongly as well as the stereochemistry of elimination.[24] In the γ position the effect of bromine as shown in Table IV is marginal.[24b] Such studies with the propyl system show that effect of substituents in the γ position are highly attenuated relative to β substituents. Both rates of halogen transfer to Cr^{II} (eq 5) as well as decomposition of the alkylchromium intermediate (eq 22) which depend on such cyclic participation are damped markedly. We conclude that participation in reaction 25 or 15 derives driving force more from stabilization due to electron delocalization or coordination than to steric forces, because of its highly selective role in 1,2 processes. In 1,3 and higher processes only those groups which participate strongly seem to continue to exert their influence by such a mechanism.

Stereochemistry of 1,3-Reductive Cyclization.—Each isomer of the pair of 2,4-dibromopentanes was separately reduced by Cr^{II} under various conditions, shown in Table VI. Reducing agents were Cr^{II}en in DMF and Cr^{II} in dimethyl sulfoxide (DMSO), which were conditions successfully employed to effect stereospecific *trans* elimination from *dl*- and *meso*-2,3-dibromobutanes.[24] These results show that under optimum conditions for stereospecificity in reductive eliminations, there is no specificity in the reductive cyclization of the homologous 2,4-dibromopentanes.

In vicinal elimination of alkyl dibromides, a 1,2-bromine bridged radical plays a key role in controlling the over-all stereochemistry of the elimination process.[24] The lack of stereospecificity in the reductive cyclization of the homologous 2,4-dibromopentanes indicates that the analogous 1,3-bromine bridged radical is unimportant (kinetically).[23c] This is also consistent with the lack of significant γ-bromine participation in the initial bromine transfer to Cr^{II} (eq 16, Y = Br; *cf.* Table V, column 3). Stereochemical integrity is, thus, lost with the formation of the 4-bromo-2-pentyl radical VI, by virtue of the absence of bridging

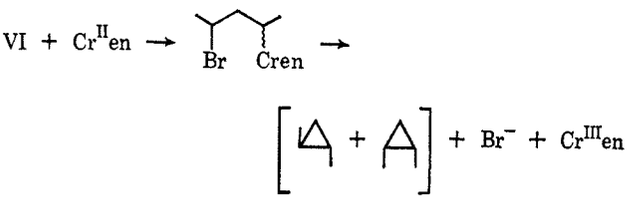


meso VI



dl (26)

by a γ-bromine. The formation of various ratios of epimeric pairs of 2-bromo-3-pentylchromium derivatives in a subsequent step will be determined by the particular Cr^{II} species extant and the solvent. These isomers can lead to different relative amounts of *cis*- and *trans*-dimethylcyclopropanes reported in Table VI.



Reductive Cyclization of Higher Homologs.—Tetramethylene dibromide and diiodide reacted readily with Cr^{II}en reagent. Only small amounts of cyclobutane were formed and protolytic reduction to *n*-butyl bromide and *n*-butyl iodide was the dominant route. The latter underwent further reduction to *n*-butane under the conditions of the experiment. Since protonolysis of the γ-iodobutylchromium intermediate is retarded

$$ICH_2CH_2CH_2CH_2I \xrightarrow[H^+]{Cr^{II}en} ICH_2CH_2CH_2CH_3 \xrightarrow[H^+]{Cr^{II}en} CH_3CH_2CH_2CH_3 \quad (27)$$

at lower acid concentrations, reduction of these dihalides was also examined at relatively high concentrations of ethylenediamine. Slightly larger amounts of

TABLE VI

REDUCTIVE CYCLIZATION OF *meso*- AND *dl*-2,4-DIBROMOPENTANE BY CHROMOUS REAGENTS[a]

2,4-Dibromopentane	Concn, *M*	Cr^{II}, *M*	en, *M*	Solvent	Dimethylcyclopropane[e] *trans*	*cis*
meso	0.0152	0.082	0.18	DMF[b]	51	49
meso	0.0154	0.083	11	DMF[c]	44	56
meso	0.0154	0.083	...	DMSO[d]	60	40
dl	0.0152	0.082	0.18	DMF[b]	50	50
dl	0.0154	0.083	11	DMF[c]	44	56
dl	0.0154	0.083	...	DMSO[d]	60	40

[a] Reactions run at room temperature. [b] 86 vol % DMF–water. [c] 22 vol % DMF–en. [d] 87 vol % DMSO–water. [e] Calculated assuming 1:1 calibration in glpc 15 ft Dowtherm A, *trans* (8.4 min), cis (12.9 min), *n*-pentane (8.2 min); *cf.* with dimethylcyclopropanes obtained from pyrazolines (R. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **87**, 3768 (1965)).

(24) (a) J. Kochi and D. Singleton, *J. Amer. Chem. Soc*, in press. (b) Neighboring-group participation alone, is not responsible for acceleration in the rate of reduction. The effect of substituents in the γ position is also, no doubt, a composite of polar and steric effects as shown by the faster reduction of γ-chloropropyl bromide and iodide compared to the corresponding butyl halide. We feel that the γ-iodo substituent exerts an effect larger than expected on the basis of comparison with γ-chloro and bromo substituents.

(25) (a) J. Leffler and J. West, *J. Org. Chem.*, **27**, 4191 (1962). See also *J. Amer. Chem. Soc.*, **80**, 5435 (1958); *J. Org. Chem.*, **26**, 733 (1961); **25**, 424 (1960); *cf.* R. Woolford and R. Gedye, *Can. J. Chem.*, **45**, 291 (1967). (b) There have also been some recent attempts to show halogen bridging from nonvicinal positions in free radicals (W. Trahanovsky and M. Doyle, *J. Org. Chem.*, **32**, 146 (1967); L. Montgomery and M. Matta, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, p 22K).

cyclobutane were formed, but still not in sufficient quantities to warrant further study.

Pentamethylene dibromide and diiodide also reacted with $Cr^{II}en$ readily, but no cyclopentane was formed. *n*-Amyl bromide and iodide were the major products, which reacted further with $Cr^{II}en$ reagent to afford *n*-pentane. In the same manner, hexamethylene dibromide and diiodide afforded only products of protolytic reduction with $Cr^{II}en$.

In the reduction of this series of polymethylene dibromides and diiodides, it is apparent that transfer of bromine or iodine to $Cr^{II}en$ produced the free radical I and ω-halopolymethylenechromium derivatives VII were generated in the usual manner. Cyclization of the latter (eq 29, $n > 1$) to cycloalkanes is not favored

$$XCH_2(CH_2)_nCH_2Cr^{2+} \xrightarrow{H^+} XCH_2(CH_2)_nCH_3 + Cr^{III} \quad (28)$$

$$XCH_2(CH_2)_nCH_2Cr^{2+} \rightarrow X^- + \begin{pmatrix}(CH_2)_n\\ CH_2{-}CH_2\end{pmatrix} + Cr^{III} \quad (29)$$

relative to protonolysis (eq 28). Barring specific effects, the probability for ring closure by internal displacements generally decreases with ring size. This is illustrated by the synthesis of methyl cyclopropyl ketone specifically from the base-catalyzed conversion of 5-chloropentanone-2.[26] Furthermore, the driving force for internal displacement of halide ion in VII is not as great as it is in organomagnesium or zinc reagents (*vide supra*). These factors, coupled with the greater proton availability in aqueous DMF solutions compared to aprotic media used in Grignard reactions, tilt the balance for competition between protonolysis (eq 28) and cyclization (eq 29) toward the former in the higher homologs.

Reduction of Trimethylene Oxide and Sulfide.—The reduction of trimethylene oxide by $Cr^{II}en$ occurred slowly at room temperature over several days. No cyclopropane or propane was liberated. *n*-Propyl alcohol was the only product found. Trimethylene sulfide reacted with $Cr^{II}en$ rapidly, but neither cyclopropane nor propane were found.

These compounds, like their lower homologs, epoxides and episulfides, probably react with $Cr^{II}en$ through the heteroatom.[13,24] The intermediate radicals generate alkylchromium compounds, which only yield products of protolytic reduction. They resemble intermediates from γ-hydroxy- and mercaptopropyl halides.

$$\square_A + Cr^{II}en \rightarrow Cr^{III}enACH_2CH_2CH_2\cdot \xrightarrow{Cr^{II}en}$$

$$Cr^{III}enACH_2CH_2CH_2Cren^{2+}$$

$$Cr^{III}enACH_2CH_2CH_2Cren^{2+} \xrightarrow{H^+} HACH_2CH_2CH_3 + Cr^{III}en$$

$$A = O, S$$

(26) (a) G. Cannon, R. Ellis, and J. Leal, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 593. (b) The methylene hydrogens are as reactive as the α-methyl hydrogens in methyl ethyl ketone toward hydroxide in aqueous dioxane (J. Warkentin and O. Tees, *J. Amer. Chem. Soc.*, **88**, 5540 (1966)). The preferential cyclization to a three- rather than five-membered ring probably derives much from entropic factors. (c) It may be possible to cyclize reductively α′α-dihalo and α,α,α′α′-tetrahalo ketones to cyclopropanones and cyclopropenones with Cr^{II}, respectively (*cf.* R. Breslow, *et al.*, *ibid.*, **87**, 1326 (1965); R. Doerr and P. Skell, *ibid.*, **89**, 4684 (1967)).

Experimental Section

Materials.—The following Eastman White Label chemicals had the physical constants listed and were used directly: 1-bromobutane, $n^{26}D$ 1.4370 (lit.[27] $n^{20}D$ 1.4398); 1-iodobutane, $n^{26}D$ 1.4970 (lit.[27] $n^{20}D$ 1.5001); 1,3-dibromopropane, $n^{24.8}D$ 1.5206 (lit.[28] $n^{20}D$ 1.5232); 1,3-dichloropropane, $n^{24.8}D$ 1.4461 (lit.[29] $n^{25}D$ 1.4362); 3-bromopropanol-1 was contaminated with approximately 12% trimethylene dibromide, $n^{24.8}D$ 1.4912 (lit.[30] $n^{20}D$ 1.4883); 3-bromopropyl phenyl ether, $n^{28}D$ 1.5441; 3-chloropropyl tosylate; trimethylene sulfide, $n^{28}D$ 1.5081.

Columbia supplied the following materials which were used without further purification: N-(3-bromopropyl)phthalimide, mp 79.5–80.0° (lit.[27] mp 72°); 3-bromopropylamine hydrobromide, mp 179–180° (lit.[31] 169–172°); 3-chloropropanol, $n^{24.8}D$ 1.4444 (lit.[27] $n^{20}D$ 1.4469); trimethylene oxide, $n^{24.8}D$ 1.3977 (lit.[27] $n^{25}D$ 1.3897) was contaminated with approximately 12% allyl chloride; 1-chloro-3-iodopropane, $n^{24.8}D$ 1.5451 (lit.[32] $n^{20}D$ 1.5472); 4-bromobutyronitrile, $n^{24.8}D$ 1.4747, was contaminated with approximately 7% trimethylene dibromide (lit.[33] $n^{20}D$ 1.4818); 1,3-dichloropropane, $n^{24.8}D$ 1.4417 (lit.[29] $n^{25}D$ 1.4362).

1,2-Dibromoethane, $n^{26}D$ 1.5353 (lit.[27] $n^{20}D$ 1.5389), and 1-bromo-3-chloropropane, $n^{24.8}D$ 1.4844 (lit.[27] $n^{20}D$ 1.4950), were from Dow and were used directly.

City Chemicals supplied 1,3-diiodopropane, $n^{24.8}D$ 1.6402 (lit.[27] $n^{20}D$ 1.6423), which was colorless and was used without further purification.

3-Bromopropyl tosylate was prepared from 3-bromopropanol-1 and tosyl chloride using Tipson's procedure:[34] bp 153–155° (0.05 mm); $n^{28}D$ 1.5345 lit.[34b] bp 130–140° (0.001 mm).

3-Bromopropyltriethylammonium bromide was prepared from trimethylene dibromide and triethylamine in ether.[21] It reacted rapidly with $Cr^{II}en$ and consumed 2.1 equiv/mol of salt (>96% assay).

meso- and *dl*-2,4-Dibromopentanes were prepared by Pritchard and Vollmer's procedure.[35] Complete separation of the cyclic sulfites was effected, but partial epimerization occurred during conversion to the dibromide: *meso* isomer, bp 50–51° (4 mm); $n^{27}D$ 1.5000; contained 88% *meso* by glpc; *dl* isomer, bp 47–48° (4.3 mm); $n^{32}D$ 1.4937; contained 93% *dl* isomer lit.[35] *meso*, $n^{20}D$ 1.5015 (95%); *dl*, $n^{20}D$ 1.4968 (98%).

Chromous perchlorate solutions were prepared as before[9] and were 0.5–0.9 *M* in strength.

Dimethylformamide (Du Pont; specified distillation range 0.6°) was used as received. Matheson Coleman and Bell ethylenediamine (98–100%) was used either neat or as a standard solution in dimethylformamide.

All operations involving chromous solutions were carried out under a helium atmosphere.

Experimental Procedure.—Solutions of the chromous–ethylenediamine reagent were prepared by addition (*via* syringe) of an aqueous chromous perchlorate solution to degassed solutions of ethylenediamine in dimethylformamide. The reagent solutions were prepared in 50- or 125-ml erlenmeyer flasks capped with rubber septa, which were secured with tightly wound rubber bands. About 0.5 mmol of as tandard solution of substrate was added by syringe to the stirred reagent. When the mixture had changed in color from royal blue to purple or red, an internal standard was added and the products were analyzed by gas chromatography. Gaseous products were sampled directly. Liquid products were analyzed by partitioning an aliquot between dilute perchloric acid and an organic solvent, followed by glpc examination of the organic layer.

The method was modified somewhat for the competition reactions, where a large (greater than tenfold) excess of organic halides was employed. A solution of the organic halides in DMF

(27) "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Co., Cleveland, Ohio, 1964–1965.

(28) C. P. Smyth and W. S. Walls, *J. Amer. Chem. Soc.*, **54**, 2266 (1932).

(29) S. S. Rossander and C. S. Marvel, *ibid.*, **50**, 1493 (1928).

(30) A. Karvonen, *Acad. Sci. Fennicae*, **5A**, 1 (1914); *Chem. Abstr.*, **14**, 2176 (1920).

(31) F. Schaefer, *J. Amer. Chem. Soc.*, **77**, 5929 (1955).

(32) W. E. Hanford and R. M. Joyce, Jr., U. S. Patent 2,440,800 (1942); *Chem. Abstr.*, **42**, 6373 (1948).

(33) L. Leclercq and A. Bruylants, *Bull. Soc. Chim. Belges*, **58**, 149 (1949).

(34) (a) J. Tipson, *J. Org. Chem.*, **9**, 239 (1944); (b) O. Hromatka, G. Stehlik, and F. Sauter, *Monatsh.*, **91**, 107 (1960).

(35) J. Pritchard and R. Vollmer, *J. Org. Chem.*, **28**, 1545 (1963).

TABLE VII
COMPETITIVE REDUCTION OF ORGANIC HALIDES WITH $Cr^{II}en$

Substrate (A)	M[b]	Substrate (B)	M	Av k_A/k_B
$CH_3CH_2CH_2CH_2Br$	0.0135	$BrCH_2CH_2CH_2Br$	0.0135	0.014
	0.0541		0.0135	0.013
	0.135		0.0135	0.017
$CH_3CH_2CH_2CH_2I$	0.00982	$ICH_2CH_2CH_2I$	0.0123	0.014
	0.0393		0.0123	0.020
	0.0982		0.0123	0.018
$BrCH_2CH_2CH_2Br$	0.0135	$BrCH_2CH_2Br$	0.0186	0.065
	0.0405		0.0186	0.066
$ICH_2CH_2CH_2I$	0.0123	$BrCH_2CH_2Br$	0.0186	1.47
	0.0221		0.0186	1.81
$ClCH_2CH_2CH_2I$	0.0177	$CH_3CH_2CH_2CH_2I$	0.0491	6.3[c]
	0.0089		0.0491	7.4[c]
	0.0089		0.0786	5.4[c]
$ClCH_2CH_2CH_2Br$	0.0185	$CH_3CH_2CH_2CH_2Br$	0.0676	13.9[c]
	0.0093		0.0676	16.4[c]
	0.0093		0.108	13.2[c]
$BrCH_2CH_2CH_2OTs$	0.00332	$CH_3CH_2CH_2CH_2I$	0.0098	1.2
	0.00133		0.0196	1.1
	0.00067		0.0491	0.98

[a] Chromous solution added rapidly by syringe to solution of halides and ethylenediamine in DMF at room temperature. [b] $[Cr(ClO_4)_2]$ 0.00518 M, ethylenediamine 0.0202 M. [c] Correction factor of 1.21 included to account for competitive reduction.

was degassed, then the requisite amount of ethylenediamine was added to the rapidly stirred mixture, followed *immediately* by the chromous solution. Various ratios of reactants were employed and relative rates determined in the usual manner. Typical data are included in Table VII.

Gas Chromatographic Data.—Ethylene, propylene, and cyclopropane were measured on a 15-ft Dowtherm A column against *n*-butane as marker (standard). A 6-ft QFI column was used to measure *n*-propyl chloride *vs.* isopropyl chloride marker.

The gases were examined using a Case-constructed instrument having a thermal conductivity detector; liquids, in solution, were measured on a Varian Aerograph A-200 equipped with flame-ionization detectors.

Registry No.—Ethylenediaminechromium(II), 15525-39-0.

Acknowledgment.—We wish to thank the National Science Foundation for a generous grant which supported this study and Mr. John Powers for the preparation of *meso*- and *dl*-2,4-pentanediols.

Structure of Diene–Phosphonous Dihalide Addition Products and of Derived Phospholenes and Phospholene Oxides[1]

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It has been shown that the cycloadducts of methylphosphonous dichloride and butadiene, isoprene, 3,4-dimethylbutadiene, or piperylene give rise to 3-phospholene oxides on hydrolysis and 3-phospholenes on reduction with magnesium. The cycloadduct from butadiene was also shown to contain the 3-phospholene ring. The 3-phospholene oxides may be caused to rearrange to 2-phospholene oxides either thermally or by refluxing aqueous base. Acid treatment was effective only for rearranging the 3-methyl derivative. The 3,4-dimethyl derivative resisted rearrangement conditions. Phenylphosphonous dibromide (synthesized by a new method from phenylphosphinic acid and phosphorus tribromide) also gave an adduct with isoprene shown by nmr studies to contain the 3-phospholene ring, which was preserved in the oxide and phospholene. However, the isoprene–phenylphosphonous dichloride adduct contained the 2-phospholene ring; the derived oxide and phospholene were also the 2 isomers. Independent syntheses of the isomeric 1-phenyl-3-methylphospholene oxides confirmed the assignments. The adduct from piperylene and phenylphosphonous dibromide also gave on hydrolysis the 3-phospholene oxide, while that from phenylphosphonous dichloride gave the 2 isomer.

The cycloaddition of conjugated dienes and phosphonous dihalides was first reported by McCormack in 1953.[2,3] The halophosphorane adducts and derived products were assumed to contain the 3-phospholene ring. It was not until 1963 that it became evident that the double bond in products derived from the adducts could appear in the 2,3 position. This behavior was first encountered among adducts from the related reaction of dienes and phosphorus trihalides,[4,5] where it was found that the trichloride gave 2-phospholene derivatives while the tribromide gave the 3 isomer. It was later stated that adducts of phenylphosphonous dichloride with isoprene or butadiene gave on hydrolysis the 2-phospholene oxides rather than the

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(2) W. B. McCormack, U. S. Patents 2,663,736 and 2,663,737 (Dec 22, 1953).

(3) The literature on this reaction has been reviewed recently: L. D. Quin, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1967, Chapter 3.

(4) U. Hasserodt, K. Hunger, and F. Korte, *Tetrahedron*, **19**, 1563 (1963).

(5) B. A. Arbuzov, A. O. Vizel, Y. Y. Sametov, and K. M. Ivanovskaya, *Dokl. Akad. Nauk SSSR*, **159**, 582 (1964).