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The Cleavage of Bonds by Low-Valent Transition Metal Ions. The Homogeneous Dehalogenation of Vicinal Dihalides by Chromous Sulfate

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The homogeneous reduction of *vic*-dihalides by chromous sulfate in aqueous dimethylformamide results in the olefin in high yield. Both allenes and appropriately substituted acetylenes (those inert to Cr^{+2}) can be obtained from the corresponding dihalides. These reductions are remarkably more rapid than the reductions of the corresponding monohalides by chromous sulfate. The stereochemistry and kinetics of the reaction are consistent with an initial homolytic scission of a carbon–halogen bond by Cr^{+2} that is assisted by a neighboring halogen.

Introduction

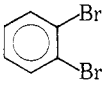
Studies of the homogeneous reduction of alkyl halides by chromous sulfate[1] have pointed up the marked rapidity of the reduction of ethylene dibromide as compared to that of unactivated primary monohalides (β-phenylethyl bromide, *n*-propyl bromide). The present work portrays the general scope and mechanism of these facile dehalogenations.

The dehalogenation of 5,6-dibromo-3-ketosteroids and 5,6-dibromosterols by $CrCl_2$ in aqueous acetone has been reported.[2] Moreover, the production of tetraphenylethylene from the reaction of diphenyldichloromethane with chromous chloride in aqueous ethanol[3] might be ascribed to the oxidation of chromous by an intermediate coupling[1,4] product 1,1,2,2-tetraphenyl-1,2-dichloroethane.

Results

Stoichiometry and Stereochemistry.—The results of the reduction of a variety of vicinal dihalides are presented in Table I. In general the reactions were carried out in 1:1 dimethylformamide–water with initial concentrations of Cr^{+2} in the range of 0.351 to 0.104 *M* and the halide at 0.111 to 0.0114 *M*. The substances are listed in a decreasing order of reactivity.

Under similar conditions the following halides were inert or very slow to react: 1,2-dichloroethane, 1,2-dibromoethylene, *o*-dibromobenzene, and *o*-diiodobenzene. The dihalopropenes were studied under conditions of stoichiometric ratios of reactants and with excess chromous sulfate. The results are portrayed in Table II. The reactivity of the dihalides toward Cr^{+2} parallels that reported for the corresponding monohalides except for the relatively slower rates of reduction of the dihalopropenes. The sequence: $PhCHBr–CH_2Br > CH_3CHBr–CHBrCH_3 > BrCH_2–CH_2Br \sim CH_2{=}CBr–CH_2Br > CH_2CHCl–CHClCH_3 >$



, $BrCH{=}CHBr$

is illustrative.

Thus, the oxidation of Cr^{+2} by vicinal dihalides produces the corresponding olefin in high yield (1).

$$-\overset{|}{\underset{Br}{C}}-\overset{|}{\underset{Br}{C}}- + 2Cr^{+2} \longrightarrow >C{=}C< + 2Cr^{+3} + 2Br^- \quad (1)$$

As noted in Table II, the 2,3-dihalopropenes yield both the allene (2a) and some of the vinylic chloride (2b) but none of the corresponding bromide.[5] With

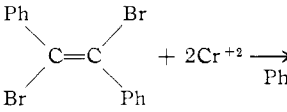
$$CH_2{=}\overset{Cl}{\underset{|}{C}}{-}CH_2Br + 2Cr^{+2} \xrightarrow{a} CH_2{=}C{=}CH_2 + 2Cr^{+3} + Br^- + Cl^- \quad (2)$$

$$\xrightarrow{b,\ H^-} CH_2{=}\overset{Cl}{\underset{|}{C}}{-}CH_3 + 2Cr^{+3} + Br^-$$

excess Cr^{+2} the product allene is reduced to propylene (3). This latter transformation resembles the reduction

$$CH_2{=}C{=}CH_2 + 2Cr^{+2} + 2H^+ \longrightarrow CH_2{=}CHCH_3 + 2Cr^{+3} \quad (3)$$

of acetylenes by this reagent.[6] Hence, the conversion (4) *should not* be considered a general reaction as to-



$$+ 2Cr^{+2} \longrightarrow PhC{\equiv}CPh + 2Cr^{+3} + Br^- \quad (4)$$

lane happens to be an acetylene that is inert to chromous sulfate. The reaction does, however, emphasize the activating influence of phenyl substituents.

The stereochemical consequence of (2) varies widely from a clean *trans* elimination (*meso*-stilbene dibromide, *meso*-2,3-dibromosuccinic acid) to the same almost thermodynamic distribution of butenes obtained from the isomeric dichlorobutanes. On the other hand, the isomeric dibromobutanes yield predominantly the *trans* elimination product but not in the same ratio. It should be noted that the composition of the butenes reported in Table I is the result of usually three independent runs. The relative yields were reproducible within 2%.

Kinetics.—The rates of disappearance of Cr^{+2} were followed by the titrimetric procedure previously described.[1] Runs at stoichiometric and nonstoichiometric ratios of reactants gave very good second-order

(1) C. E. Castro and W. C. Kray, Jr., *J. Am. Chem. Soc.*, **85**, 2768 (1963).
(2) P. L. Julian, W. Cole, A. Magnani, and E. W. Meyer, *ibid.*, **67**, 1728 (1945).
(3) J. F. Neumer and S. Aktipis, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., 1961, p. 9Q.
(4) C. E. Castro, *J. Am. Chem. Soc.*, **83**, 3262 (1961).
(5) Although the total yield of products does not account for all of the Cr^{+2} consumed, if significant amounts of 2-bromopropene were produced, the substance should have been detected.
(6) C. E. Castro and R. D. Stephens, *J. Am. Chem. Soc.*, **86**, 4358 (1964).

TABLE I

PRODUCTS OF THE REDUCTION OF VICINAL DIHALIDES BY CHROMOUS SULFATE AT ROOM TEMPERATURE

Alkyl halide	Cr^{+2} stoichiometry	Product distribution	Conversion,[a] %	Yield (calcd.),[b] %	Reactivity
(1,2-Dibromoethyl)benzene	2	Styrene	86	92	
(1-Chloro-2-bromoethyl)benzene	2	Styrene	75	93	
(1,2-Dichloroethyl)benzene	2	Styrene	88	91	
meso-α,β-Dibromosuccinic acid[d]	2	Fumaric acid	95	92	Rapid
meso-2,3-Dibromobutane	2	76% 24%	86	99	5–30 min. to completion
dl-2,3-Dibromobutane	2	35%  65%	88	99	
1,2-Dibromo-3-chloropropane[e]	2	Allyl chloride	100	110	
		Propylene	99	97	
Ethylene dibromide[c]	2	Ethylene	93	100	
dl-erythro-2-Chloro-3-iodobutane	(2)[f]	74% 26%	83		
dl-threo-2-Chloro-3-iodobutane	(2)	59% 41%	82		
1,2-Dichloro-3-butene	(2)	1,3-Butadiene	68	68	Moderate 1–4 hr. to the conversion indicated
Hexachloroethane	(2)	Tetrachloroethylene	47	45	
meso-2,3-Dichlorobutane	(2)	71% 29%	44	57	Slow
dl-2,3-Dichlorobutane	(2)	72%  28% 	49	56	2 days to the conversion indicated
meso-Stilbene dibromide	2	*trans*-Stilbene	100	101	Unknown
trans-Tolane dibromide	2	Tolane	99	97	I.c., rapid but heterogeneous

[a] Conversion to indicated products. [b] Yields based on Cr^{+2} stoichiometry. [c] Taken from ref. 1. [d] Solvent water. [e] Solvent 1:2 DMF–H_2O; the reduction of intermediate allyl chloride proceeds with moderate reactivity. [f] (Inferred stoichiometry).

TABLE II

PRODUCTS OF THE REDUCTION OF THE 2,3-DIHALOPROPENES BY CHROMOUS SULFATE

Halide	Ratio of concn. $(Cr^{+2})_0/(RX_2)_0$	Product distribution, %[a] $CH_2{=}CHCH_3$	$CH_2{=}C{=}CH_2$	$CH_2{=}C(Cl){-}CH_3$	Conversion, %	Yield,[b] %
$CH_2{=}C(Br){-}CH_2{-}Br$	5.4	74	26		79	81
	2.0	2	98		83	65
$CH_2{=}C(Br){-}CH_2{-}Cl$	5.4	78	22		79	85
	2.0	5	95		83	70
$CH_2{=}C(Cl){-}CH_2Cl$	5.4	52	37	11	77	81
	2.0	4	81	15	61	64
$CH_2{=}C(Cl){-}CH_2Br$	5.4	68	21	11	77	80
	2.0	2	82	16	61	64

[a] The total allene produced is equal to allene plus propylene. Propylene was shown to result from allene with excess Cr^{+2}. [b] Based on a stoichiometry of 2 for the formation of 2-chloropropene and 2 for the conversion of product allene to propylene.

plots through 90% completion. A typical run is presented in Fig. 1.

$$\text{rate} = k_2(Cr^{+2})(RX_2)$$

All rate runs were in 1:1 dimethylformamide–water with concentrations of Cr^{+2} and dihalide ranging from 0.0126 to 0.0220 M and 0.00725 to 0.0111 M, respectively. Perchloric acid was used to set the ionic strength at 1.0. The second-order rate constants for reduction of the 2,3-dihalopropenes and the (1,2-dihaloethyl)benzenes are compared with those of allyl chloride and (1-chloroethyl)benzene in Table III. The rapid reduction of *meso*-2,3-dibromobutane is to be contrasted with the much slower conversion of *t*-butyl bromide to isobutane.[1] Under conditions in which the vicinal dihalides are converted to the olefin, allyl chloride and (1-chloroethyl)benzene are quantitatively converted to propylene and 2,3-diphenylbutane.[1] The deviations expressed in Table III represent the reproducibility of the rate constants assessed from at least three independent runs.

TABLE III

RATES OF REDUCTION OF HALIDES BY CHROMOUS SULFATE AT 29.7°, $\mu = (HClO_4) = 1.0$

Halide	k_2, l./mole/min.
Allyl chloride[a]	1.2 ± 0.1
2,3-Dichloropropene	2.2 ± .1
2-Bromo-3-chloropropene	2.6 ± .1
meso-2,3-Dibromobutane	18 ± 2
(1-Chloroethyl)benzene[a]	2.3 ± 0.8
(1,2-Dichloroethyl)benzene	46 ± 3
(1-Chloro-2-bromoethyl)benzene	95[b]

[a] Taken from ref. 1. [b] An estimate from a second-order plot. The first point at 2 min. was at 72% completion.

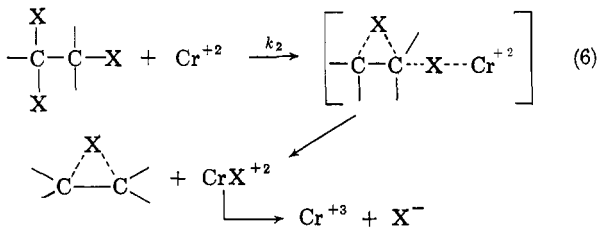
Discussion

The Initial Scission.—The most striking feature of the reduction of vicinal dihalides by Cr^{+2} is the enhanced speed of the reaction as compared to the reduction of similarly substituted monohalides. Some idea of the enhanced rates for the process can be obtained from Table III, but perhaps a more impressive comparison would be that of ethylene dibromide with *n*-propyl bromide. Thus with concentrations of ~0.3 *M* Cr^{+2} and ~0.06 *M* organic halide, 80% of the dihalide is consumed in ~10 min. while the monohalide is consumed to the extent of only 25% in 1.5 days.

We rationalize our findings by a mechanism analogous to that advocated for the reduction of monohalides in which an initial rate-determining scission to a radical occurs (5). In the present case, we ascribe the acti-

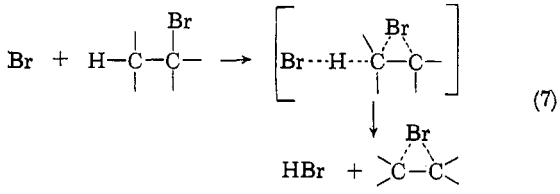
$$RX + Cr^{+2} \longrightarrow CrX^{+2} + R\cdot \qquad (5)$$

vating influence of an adjoining halogen to its ability to function as a *neighboring group* in assisting the initial cleavage to result in a halogen-bridged radical (6).



(6)

This suggestion is consistent with recent studies of the photobromination of alkyl halides in which a halogen-bridged radical has been implicated. Thus, the observation that bromine atoms primarily attack alkyl bromides on the carbon adjacent to the one bearing halogen, in spite of unfavorable polar effects, has been attributed to a participation of the carbon-bonded bromine in the hydrogen abstraction step[7] (7). Moreover, the free-radical bromination of (+)-1-bromo-2-



(7)

methylbutane and (+)-1-chloro-2-methylbutane selectively yields (−)-1,2-dibromo-2-methylbutane and (−)-2-bromo-1-chloro-2-methylbutane, respectively[8]—a manifestation of the bridged radicals to maintain stereochemical integrity until they can react with bromine. The attack of Cr^{+2} on a vicinal dihalide (6) very nearly approximates the microscopic reverse of the collision of a bridged bromine radical with molecular bromine. Finally an investigation of the e.p.r. spectra resulting from the addition of bromine atoms to olefins suggests a bridged symmetrical structure for bromoalkyl radicals.[9]

A comparison of the rates of reduction of the 2,3-dihalopropenes and the (1,2-dihaloethyl)benzenes lends strong support to the contention of neighboring group participation in these reactions. Thus, because an

(7) W. Thaler, *J. Am. Chem. Soc.*, **85**, 2607 (1963).
(8) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2850 (1963).
(9) P. I. Abell and L. H. Piette, *ibid.*, **84**, 916 (1962).

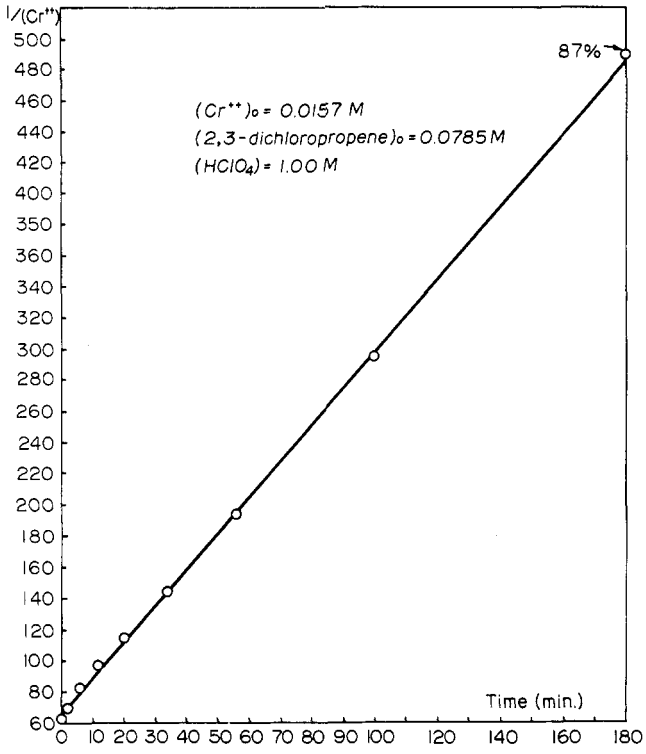
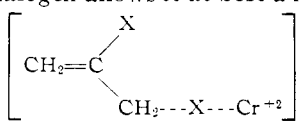


Figure 1.

allylic or benzylic halogen is far more easily removed by Cr^{+2} than either a vinylic or β-phenylalkyl halide, an assessment of the capacity of a neighboring halogen to assist the initial scission can be made. Thus, from the ratio $k_{(1,2\text{-dichloroethyl})\text{benzene}}/k_{(1\text{-chloroethyl})\text{benzene}}$ an adjacent chlorine facilitates the rupture of a benzylic chlorine by a factor of ~20. In keeping with the free-radical halogenation studies cited above, a bridging bromine would be expected to stabilize the incipient benzylic radical more effectively, and $k_{(1\text{-chloro-2-bromoethyl})\text{benzene}}/k_{(1\text{-chloroethyl})\text{benzene}}$ is ~50.

By contrast, the relative insensitivity of the rates of reaction of the allylic chlorides to a neighboring halogen substituent on the vinylic carbon appears remarkable. Moreover, allyl chloride, 2,3-dichloropropene, and 2-bromo-3-chloropropene, despite the lability of allylic halides toward Cr^{+2}, are slower to react than 2,3-dibromobutane. These findings are quite compatible with the suggested mechanism and lend support to it, for in these cases the more rigid sp^2–p bonding of the vinylic halogen allows it at best a muted capacity



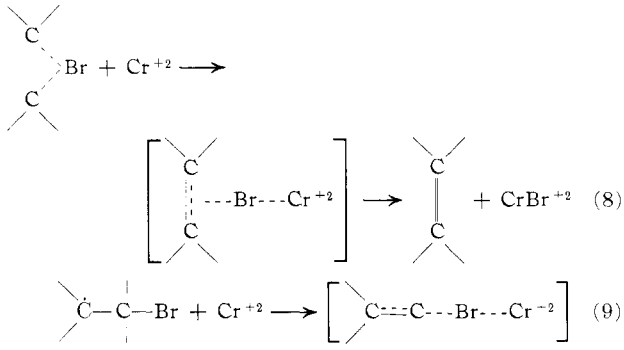
to function as a neighboring group. Hence the 2,3-dihalopropenes react with Cr^{+2} at a rate not very different from allyl chloride.

The loose bonding of halogen in an α-haloalkyl radical is manifest in the rearrangement of bromine and chlorine in bromo-[10] and chloro-[11] alkyl radicals and in the reversible addition of halogen atoms to olefins.[12]

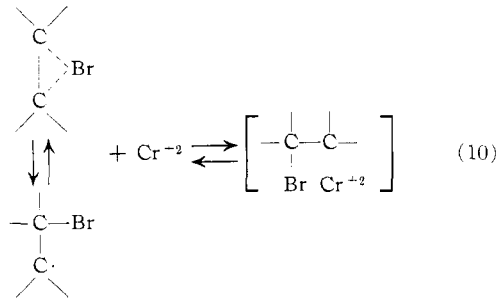
(10) P. S. Skell, R. G. Allen, and N. D. Gilmour, *ibid.*, **83**, 504 (1961); for a recent summary, *cf.* ref. 9 and references therein.
(11) Chlorine migrations in free radicals have been advocated for some time: C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 268 and 296. Recent reports indicate the process is less facile with chlorine than bromine: ref. 8, footnote 7.
(12) B. A. Bohm and P. I. Abell, *Chem. Rev.*, **62** 608 (1962), and references therein.

It might then be expected that an α-haloalkyl radical should rapidly lose a halogen atom to Cr^{+2}.

Removal of the Second Halogen.—The attack of Cr^{+2} upon an α-haloalkyl radical can be depicted in a variety of ways. For example, Cr^{+2} may withdraw a halogen atom from a bridged radical (8) or its open chain tautomer (9). Alternately, Cr^{+2} may reversibly

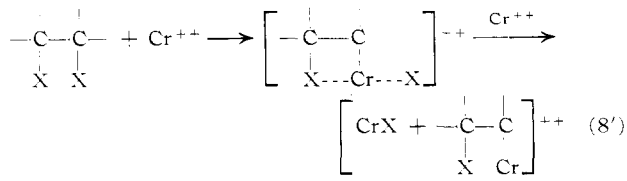


affiliate with carbon (10) to produce an intermediate



RCr^{+2} bearing an α-halogen. Such an intermediate ion would be analogous to $PhCH_2Cr(H_2O)_5^{+2}$ and $Cl_2CHCr(H_2O)_5^{+2}$ which have been prepared in solution.[13] The importance of these ions in the path of reduction of monohalides by Cr^{+2} has been noted.[1] Once formed,[14a] the ion may dissociate (11) by: (a) a *cis* elimination of CrX^{+2}, (b) a *trans* elimination of Cr^{+3} and X^-, or (c) a proton transfer from the solvation sphere of the metal ion resulting in haloalkane (alkene).[14b]

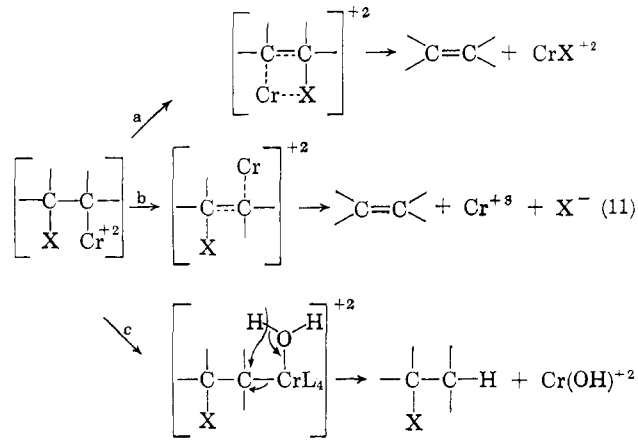
The wide range of stereochemical results accords with a multiplicity of paths of reaction of the second Cr^{+2} with the radical produced from the first attack. Thus the clean *trans* elimination of *meso*-2,3-dibromosuccinic acid[15] is most easily rationalized by path 6 followed by 8.



not be eliminated, that is to say, whether or not the attack of the second Cr^{+2} should be formulated as an approach to a free radical (as it is above in eq. 8–10) or as rapid withdrawal of a halogen ligand from a Cr^{+3} complex (8′) is unresolved; for a discussion on this point see ref. 1. (b) Path 11c for the reduction of allylic radicals has been detailed; *cf.* ref. 1.

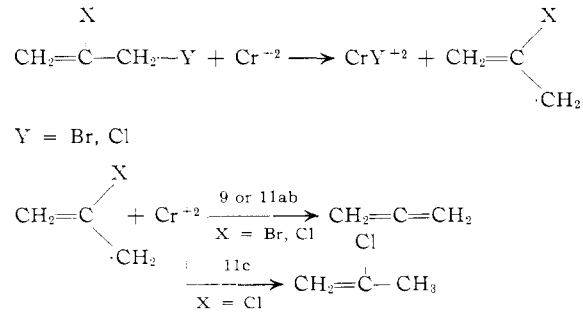
(15) Unfortunately, because of low solubilities, the long reaction times employed for the reduction of stilbene dibromide allows for the isomerization of *cis*- to *trans*-stilbene. Thus, a 4-day reduction of *dl*-stilbene dibromide yields predominantly *trans*-stilbene. Similar results have recently been reported for the $LiAlH_4$ reduction of the stilbene dibromides and the *cis–trans* isomerization of the olefins: J. F. King and R. G. Pews, *Can. J. Chem.*, **42**, 1294 (1964). However, under reaction conditions identical with the reduction of dibromosuccinic acid, maleic acid is not isomerized.

(16) H. Lux and G. Illman, *Ber.*, **91**, 2148 (1958).



The predominant "*trans* character" of the elimination of halogen from the dibromobutanes is consistent with a greater stability for a *trans* (methyl) bridged radical than a *cis* one, whereas with the corresponding dichlorides, the radical resulting in the first step of reaction is free to racemize and be subsequently reduced by paths 9, 10, or 11.

It is significant that the allylic halogen of the 2,3-dihalopropenes controls the rate of reaction of these halides with Cr^{+2} but has no influence upon the distribution of products. The product composition is determined by the halogen in the vinylic position (Table II). Hence, like the initial scission, the removal of chlorine in the second attack of Cr^{+2} is more difficult than the removal of bromine.



Experimental

All operations involving Cr^{+2} solutions were carried out in a nitrogen atmosphere.

Materials.—Chromous sulfate solutions were prepared by the zinc powder reduction of $Cr_2(SO_4)_3 \cdot 5H_2O$ in the manner previously described.[1] Transfers and storage of this solution and analyses for Cr^{+2} were handled in like fashion. The solutions employed in this work were 0.30–0.70 *M*.

Solid chromous sulfate pentahydrate was prepared for use in the kinetic studies by the method of Lux and Illman.[16] The crystals were stored in a dry nitrogen atmosphere and were transferred in the air without significant decomposition.

The physical properties of the following substances checked with those of the literature and they were employed without purification: Eastman Kodak White Label 1,2-dibromoethane, 1,2-dichloroethane, 1,2-dibromoethylene, *o*-dibromobenzene, *o*-diiodobenzene, and Matheson Coleman and Bell α,β-dibromosuccinic acid and hexachloroethane. The following materials were freshly distilled before use and their physical properties were those of the literature: 1,2-dichloro-3-butene, 2,3-dibromopropene, 2,3-dichloropropene, 2-bromo-3-chloropropene, and di-

methylformamide (DMF). (1,2-Dibromoethyl)benzene was recrystallized from an ethanol–water solution (m.p. 71.5°) before use. *meso*-2,3-Dibromobutane was prepared by bromination of *trans*-2-butene in carbon tetrachloride; b.p. 60° (26 mm.), $n^{25}D$ 1.5088 (lit.[17] $n^{25}D$ 1.5092). *dl*-2,3-Dibromobutane was prepared by bromination of *cis*-2-butene in carbon tetrachloride; b.p. 60° (24 mm.), $n^{20}D$ 1.5143 (lit.[17] $n^{20}D$ 1.5147). *meso*-2,3-Dichlorobutane was prepared by chlorination of *trans*-2-butene at −20° by the method of Lucas and Gould[18]; b.p. 49° (80 mm.), $n^{26}D$ 1.4372 (lit.[18] b.p. 49.5° (80 mm.), $n^{25}D$ 1.4386).

dl-2,3-Dichlorobutane was prepared in a similar manner from *cis*-2-butene; b.p. 52–53° (80 mm.), $n^{22}D$ 1.4417 (lit.[18] b.p. 53° (80 mm.), $n^{25}D$ 1.4409). *dl-erythro*-2-Chloro-3-iodobutane was prepared from *dl-trans*-2,3-epoxybutane by the method of Lucas and Garner.[19] The epoxide was treated with HI and the resulting iodoalcohol was treated with concentrated HCl giving the desired iodochloride, b.p. 29° (5 mm.), $n^{20.5}D$ 1.5338 (lit.[19] b.p. 35° (5 mm.), $n^{25}D$ 1.5312). *dl-threo*-2-Chloro-3-iodobutane, b.p. 36° (5 mm.), $n^{21.5}D$ 1.5356 (lit.[19] b.p. 33° (4 mm.), $n^{25}D$ 1.5337), was prepared in a similar manner from *cis*-2,3-epoxybutane.[19] 1,2-Dibromo-3-chloropropane was prepared by bromination of allyl chloride. (1-Chloro-2-bromoethyl)benzene was prepared by treating styrene with N-bromoacetamide and HCl as described by Buckels and Long[20]; b.p. 108–110° (7 mm.), $n^{23}D$ 1.5765 (lit.[20] b.p. 110–114° (7 mm.), $n^{20}D$ 1.5770). (1,2-Dichloroethyl)benzene was prepared by chlorination of styrene at 0° in chloroform[21]; b.p. 111° (15 mm.), $n^{20}D$ 1.5520 (lit.[21] b.p. 114.5–115.5° (15 mm.), $n^{15}D$ 1.5544). *trans*-Tolane dibromide was prepared by bromination of tolane in ether and recrystallized from ethanol; m.p. 209° (lit.[22] 211°). *meso*-Stilbene dibromide was prepared by bromination of *trans*-stilbene in ether; m.p. 240° (lit.[23] 241–242°). 2-Chloro-3-bromopropene was prepared by treating 2,3-dichloropropene with NaBr in DMF at 50° for 8 hr.[24]; b.p. 56° (80 mm.), $n^{22}D$ 1.5029 (lit.[25] b.p. 55° (79 mm.), $n^{20}D$ 1.505).

Kinetic Studies.—Cr^{+2} was followed titrimetrically using the rapid sampling technique and analytical procedure previously described.[1] In each case solid $CrSO_4 \cdot 5H_2O$ was dissolved in 50% aqueous dimethylformamide (v./v.) and sufficient perchloric acid was added to make the solution 1.0 *F* in acid. The substrate was dissolved in the same solvent system and after temperature equilibration the run was commenced. In the initial runs, stoichiometric initial concentrations of reactants were used. The over-all order of the reaction was determined to be 2 from plots of concentration *vs.* time using the fractional-life period method.[26] Rate constants were evaluated graphically from plots of $1/(Cr^{+2})$ *vs.* time. In subsequent runs, the order with respect to each reactant and the rate constants were determined from plots of log $(Cr^{+2})/(\text{substrate})$ *vs.* time when nonequivalent initial concentrations were employed.

The Cr^{+2} Reductions.—The technique used in these reactions was like that previously described.[1] All reactions producing gaseous products were carried out at reduced pressure (~60 mm.) and gas evolution was measured manometrically. The products were identified by gas chromatography on a 30-ft. dimethylsulfolane column and by their infrared spectrum. When several products were produced, their concentrations were determined by integrating the gas chromatographic peaks. All reactions producing liquid or solid products were carried out under a positive pressure of nitrogen. The products were isolated and identified as described. All reactions were run at room temperature.

***meso*-2,3-Dibromobutane** (1.7352 g., 0.00804 mole) in 50 ml. of DMF was treated with 50 ml. of 0.502 *M* Cr^{+2} (0.0251 mole). After several hours, 0.0140 mole of Cr^{+2} was consumed and 0.00691 mole of 2-butene (76% *trans*, 24% *cis*) was produced. Under the reaction conditions, neither *trans*- nor *cis*-2-butene was isomerized after exposure for 1 day.

***dl*-2,3-Dibromobutane** (1.7245 g., 0.00800 mole) in 50 ml. of DMF was treated with 50 ml. of 0.470 *M* Cr^{+2} (0.0235 mole). After several hours, 0.0142 mole of Cr^{+2} was consumed and 0.00701 mole of 2-butene (65% *cis*, 35% *trans*) was produced.

***meso*-2,3-Dichlorobutane** (0.8015 g., 0.00631 mole) in 50 ml. of DMF was treated with 50 ml. of 0.311 *M* Cr^{+2} (0.0156 mole). After 4 days, 0.00980 mole of Cr^{+2} was consumed and 0.00276 mole of 2-butene (71% *trans*, 29% *cis*) was produced. Gas chromatographic analysis (DC-710 column) of both a steam distillate and an ether extract of the reaction mixture showed only starting dichloride. No further attempts were made to isolate other possible products.

***dl*-2,3-Dichlorobutane** (0.8051 g., 0.00634 mole) in 100 ml. of DMF was treated with 100 ml. of 0.311 *M* Cr^{+2} (0.0311 mole). After 7 days, 0.0113 mole of Cr^{+2} was consumed and 0.00313 mole of 2-butene (72% *trans*, 28% *cis*) was produced. Only starting dichloride (v.p.c.) could be detected by distillation or ether extraction. No further attempts were made to isolate other possible products.

***dl-erythro*-2-Chloro-3-iodobutane** (2.1842 g., 0.0100 mole) in 100 ml. of DMF was treated with a solution of 50 ml. of H_2O and 50 ml. of 0.652 *M* Cr^{+2} (0.0326 mole). After several hours, 0.00829 mole of 2-butene (74% *trans*, 26% *cis*) had been produced. The amount of Cr^{+2} consumption was not determined because the analysis was impaired by the presence of iodide.

***dl-threo*-2-Chloro-3-iodobutane** (2.1872 g., 0.0100 mole) in 100 ml. of DMF was treated with a solution of 50 ml. of H_2O and 50 ml. of 0.652 *M* Cr^{+2} (0.0326 mole). After several hours, 0.00816 mole of 2-butene (59% *trans*, 41% *cis*) was produced. Again Cr^{+2} consumption was not analyzed.

1,2-Dibromo-3-chloropropane (2.0794 g., 0.00880 mole) in 100 ml. of DMF was treated with 100 ml. of 0.450 *M* Cr^{+2} (0.0450 mole). The reaction was allowed to proceed overnight. Propylene (0.00875 mole) was produced and 0.0360 mole of Cr^{+2} was consumed. In a second reaction, 4.0925 g. (0.0173 mole) of 1,2-dibromo-3-chloropropene in 100 ml. of DMF was treated with a solution of 50 ml. of H_2O and 50 ml. of 0.692 *M* Cr^{+2} (0.0346 mole). After 1 day, all the Cr^{+2} was consumed and 0.00179 mole of propylene and 0.0155 mole of allyl chloride was produced. No allyl bromide could be detected (by v.p.c.) either in the gas phase or the reaction mixture.

1,2-Dichloro-3-butene (1.2518 g., 0.0100 mole) in 100 ml. of DMF was treated with a solution of 100 ml. of H_2O and 100 ml. of 0.656 *M* Cr^{+2} (0.0656 mole). After 1 day, 0.0197 mole of Cr^{+2} was consumed and 0.00675 mole of 1,3-butadiene was produced. No other products could be detected by gas chromatographic analysis (10-ft. Carbowax column at 95°) of the reaction mixture. No further attempts were made to isolate other possible products.

2,3-Dibromopropene, 2-bromo-3-chloropropene, 2,3-dichloropropene, and 2-chloro-3-bromopropene were all treated with Cr^{+2} under identical conditions. Typically, 0.0120 mole of dihalide in 100 ml. of DMF was treated with 100 ml. of 0.652 *M* Cr^{+2} (0.0652 mole). In each case a second reaction was run in which 0.0163 mole of dihalide in 100 ml. of DMF was treated with a solution of 50 ml. of H_2O and 50 ml. of 0.652 *M* Cr^{+2} (0.0326 mole). The results are presented in Table III.

(1,2-Dibromoethyl)benzene (2.6404 g., 0.0100 mole) in 100 ml. of DMF was treated with 100 ml. of 0.701 *M* Cr^{+2} (0.0701 mole). The homogeneous reaction was very fast. After standing overnight, 0.0188 mole of Cr^{+2} was consumed. The reaction mixture was extracted with ether and the ether extract was then washed with water to remove any DMF present in the extract. The ether extract was then dried over anhydrous Na_2SO_4, concentrated to a small volumn, and analyzed by gas chromatography on a 10-ft. Carbowax column at 120°. In this way 0.00864 mole of styrene was detected using toluene as an internal standard. The peak corresponding to styrene was trapped and found to have $n^{22}D$ 1.5468 and an infrared spectrum identical with known styrene.

(1-Chloro-2-bromoethyl)benzene (2.1949 g., 0.0100 mole) in 100 ml. of DMF and 50 ml. of H_2O was treated with 50 ml. of 0.678 *M* Cr^{+2} (0.0339 mole). The homogeneous reaction was very fast. After 4.5 hr. 0.0161 mole of Cr^{+2} had been consumed and 0.00750 mole of styrene had been produced.

(1,2-Dichloroethyl)benzene (1.7500 g., 0.0100 mole) in 100 ml. of DMF and 50 ml. of H_2O was treated with 50 ml. of 0.678 *M* Cr^{+2} (0.0339 mole). The homogeneous reaction was very fast. After standing overnight, 0.0194 mole of Cr^{+2} had been consumed and 0.00880 mole of styrene had been produced.

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trans-**Tolane Dibromide** (1.3520 g., 0.00400 mole) in 125 ml. of DMF was added to a solution of 50 ml. of DMF, 125 ml. of H_2O, and 50 ml. of 0.690 *M* Cr^{+2} (0.0345 mole). Upon mixing the reactants, much of the dibromide came out of solution and the solution remained heterogeneous during the reaction. After 3 days, 0.00820 mole of Cr^{+2} had been consumed. The reaction mixture was diluted with 350 ml. of H_2O and filtered. The crystals were washed with H_2O and dried and the filtrate was extracted with ether. The ether extract was washed with H_2O to remove DMF, dried over anhydrous Na_2SO_4, and evaporated. The combined crystals provided 0.7063 g. (0.00397 mole, 97%) of tolane, m.p. 59–59.5°, m.m.p. 59–59.5° (lit.[27] 60°). The infrared spectrum was identical with that of a known sample.

meso-**Stilbene dibromide** (1.360 g., 0.00400 mole) in 125 ml. of DMF was added to a solution of 50 ml. of DMF, 125 ml. of H_2O, and 50 ml. of 0.701 *M* Cr^{+2} (0.0351 mole). Upon mixing the reactants, much of the dibromide came out of solution and the solution remained heterogeneous during the reaction. After 3 days, 0.0080 mole of Cr^{+2} had been consumed. Dilution of the reaction mixture with H_2O, filtration, and ether extraction provided 0.7270 g. (0.00404 mole) of *trans*-stilbene, m.p. 123–124°, m.m.p. 123–124° (lit.[28] 124°). The infrared spectrum was identical with that of a known sample. No *cis*-stilbene was isolated.

meso-α,β-**Dibromosuccinic acid** (4.1414 g., 0.0150 mole) in 200 ml. of H_2O was treated with 100 ml. of 0.311 *M* Cr^{+2} (0.0311 mole). The reaction was quite rapid. After standing overnight, 0.0308 mole of Cr^{+2} had been consumed. The reaction mixture was basified with solid KOH and the $Cr(OH)_3$ precipitate was filtered off, dissolved in a minimal amount of concentrated H_2SO_4, and extracted with ethyl acetate. The reaction mixture was acidified and extracted with ethyl acetate. The combined extracts provided 1.65 g. (0.0142 mole) of fumaric acid, m.p. 280–282° (sealed tube). The infrared spectrum was identical with a known sample. No maleic acid was found. Under these reaction conditions maleic acid was not isomerized.

Hexachloroethane (2.3700 g., 0.0100 mole) in 100 ml. of DMF was added to a solution of 50 ml. of DMF, 50 ml. of H_2O, and 100 ml. of 0.690 *M* Cr^{+2} (0.0690 mole). The homogeneous reaction mixture turned green (Cr^{+3}) immediately. After 24 hr., 0.0210 mole of Cr^{+2} had been consumed. The reaction mixture was diluted with H_2O and extracted with ether. The ether extract was dried, concentrated, and analyzed by gas chromatography (DC-710 column). The product was identified as tetrachloroethylene by its retention time and its infrared spectrum. Quantitative recovery was not effected.

The following compounds were scanned[1] for reactivity with Cr^{+2} and were found to be inert: 1,2-dichloroethane, 1,2-dibromoethylene, *o*-dibromobenzene, and *o*-diiodobenzene.

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[CONTRIBUTION FROM THE ORGANIC CHEMICAL RESEARCH SECTION, LEDERLE LABORATORIES DIVISION, AMERICAN CYANAMID CO., PEARL RIVER, NEW YORK]

A Novel Pyrrolo[1,2-*a*]indole Rearrangement

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Treatment of 1-keto-1H-pyrrolo[1,2-*a*]indoles I and VII with oxalyl chloride afforded products II and IX, respectively, in which the 1H-pyrrolo[1,2-*a*]indole system had rearranged to a 9H-pyrrolo[1,2-*a*]indole system, the 1-keto group was replaced by a 1-chloro group, and 3-oxalyl substituents were introduced. The nature of this rearrangement is discussed and further transformations of the products are described.

In the course of a study[1] concerned with the introduction of a potential hydroxymethyl substituent at the 9-position of the 1-ketopyrroloindole system (I), we investigated the reaction of this system with oxalyl chloride. The reaction of 3-unsubstituted indoles with this reagent is a common method for functionalization of the 3-position[2] and, since oxalyl chloride is a strong electrophile, its reaction with the partially deactivated I was considered feasible.[2] However, treatment of I with this reagent did not proceed in the anticipated manner, and instead a novel rearrangement occurred. This rearrangement and subsequent substitution into the rearrangement product are the subject of the present paper.

When ketone I[3] was treated with 1 mole of oxalyl chloride in methylene chloride at 5°,[2] little reaction occurred and impure starting material was recovered. However, treatment of I with 2 moles of oxalyl chloride gave a good conversion of I to a noncrystalline substance which on treatment with methanol afforded yellow compound II, $C_{21}H_{16}NO_4Cl$, the chlorine of which was not reactive to silver nitrate. Infrared and n.m.r. indicated the presence of a methoxalyl group and the absence of the 1-keto function in this substance. Reduction of II with sodium borohydride gave a white compound IV, $C_{21}H_{18}NO_4Cl$, in which the ketonic carbonyl of the oxalyl group had apparently been reduced. The ultraviolet absorption spectrum of IV had a single maximum at 271 mμ, which position was lower than that of any indole we had hitherto encountered. We therefore considered the strong possibility that II and IV were not 1H-2,3-dihydropyrroloindoles (indole chromophores) but were the result of rearrangement to a different system. A fairly close match to the ultraviolet absorption spectrum of IV was provided by that of 9H-pyrroloindole V (N-phenylpyrrole chromophore, λ_{max} 265 mμ) reported by Laschtuvka and Huisgen.[4]

In order to obtain further evidence for the supposition that II and IV were members of the 9H-pyrroloindole series substituted with a methoxalyl and a reduced methoxalyl group, respectively, 7-benzyloxy-9H-pyrroloindole (VI)[5] was treated with oxalyl chloride in methylene chloride, followed by the addition of methanol. This treatment afforded yellow methoxalyl derivative VIII, which showed an ultra-

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