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STEREOCHEMISTRY OF Cr(II) REDUCTIONS

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Alkyl halides can be reduced to the corresponding hydrocarbons by the use of salts of Cr(II) (1). Two important extensions of this reaction have been developed by Kochi, *et al.* (2) and Barton, *et al.* (3). Kochi and co-workers used complexing agents such as ethylenediamine to extend the scope of the reaction to include normally unreactive halides such as primary chlorides (2). Barton, *et al.* have shown that bromo alcohols and similar derivatives which normally undergo reductive elimination reactions on treatment with Cr(II) (4) are reduced in good yields when hydrogen donors such as 1-butanethiol are present (3).

No study has been made on the relative stereochemistry of normal Cr(II) reductions of halides versus reductions with Cr(II) in the presence of hydrogen donors. Our interest in this matter stems both from the obvious mechanistic possibilities that stereoselectivity for the two types of reduction might differ and thus be of possible synthetic utility and from our major research interest of comparing the stereochemistry of several types of reductions with the stereochemistry of electroreductions (5).

In this communication we present the stereochemical results of the Cr(II)-ethylenediamine reductions (both with and without added 1-butanethiol) on *cis*- and *trans*-4-*t*-butyl-1-chloro-1-methylcyclohexane (Ia and Ib).

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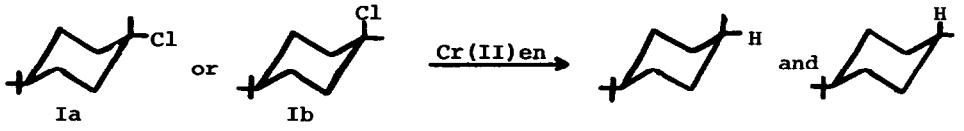

The chlorides were prepared from the corresponding alcohols by the method of Brown, *et al.* (6) and purified by preparative gas chromatography. Reductions were carried out using known literature methods (2,3) and analysis of products was carried out gas chromatographically on a 8% QF-1 on 60/80 Chrom G column using the internal standard method. Table I lists the stereochemical results of the investigation.

TABLE I

Stereochemistry of Cr(II)(en) Reductions

4-*t*-Butyl-1-Methyl-1-Chloro Cyclohexane	Reaction Conditions	% *trans*	% *cis*	% yield*
81.3% *trans* chloride	18 hr reaction time	46.0	54.0	40
81.3% *trans* chloride	6 hr reaction time	41.9	58.1	18
98.0% *trans* chloride	18 hr reaction time	41.0	59.0	82
98.0% *trans* chloride	30 min reaction time	35.1	64.9	67
84.7% *cis* chloride	18 hr reaction time	35.5	64.5	36
92.0% *cis* chloride	30 min reaction time	31.0	69.0	69
98.0% *trans* chloride	1-butanethiol added before reaction begun	92.0	8.0	90
92.0% *cis* chloride	1-butanethiol added before reaction begun	90.0	10.0	96

It will be noted that the stereochemistry of the reductions differ markedly, with normal reductions yielding predominant amounts (62 ± 8%) of *cis*-4-*t*-butyl-1-methyl cyclohexane from either Ia or Ib while the presence

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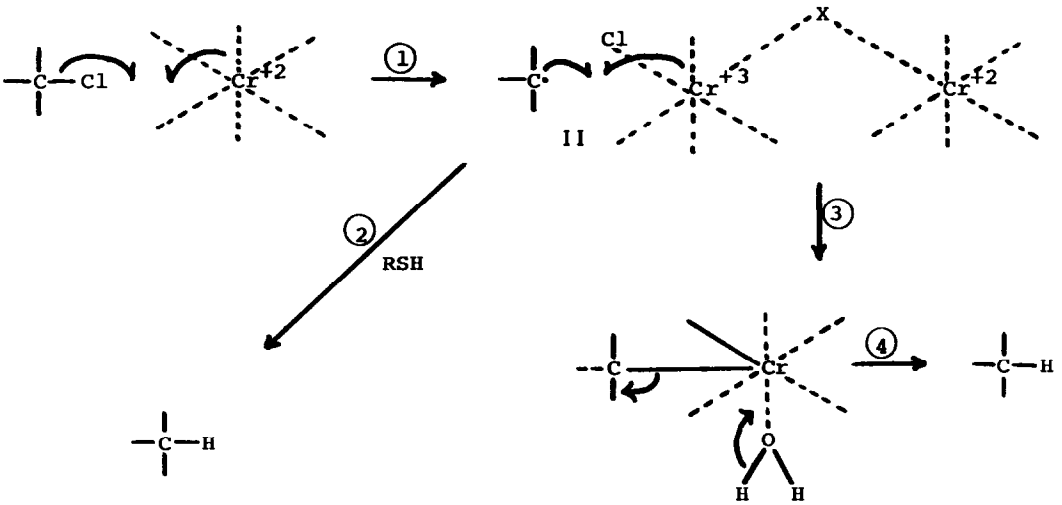
*Includes approximately 8% of 4-*t*-butyl-1-methyl cyclohexene for each run.

of a hydrogen donor leads to an excess of the more stable *trans* isomer (91 ± 1%) from either isomer of the starting material.

As the results in Table I indicate, some difficulty was encountered in obtaining reproducible results in the isomer ratio employing normal reaction conditions. Although experimental parameters (time of reaction and concentration of reactants) were varied, the set of data is too limited at present for speculation as to the cause for these reasonably slight differences in *cis*:*trans* ratios. We also showed that the alkene which was always a minor product in the reactions was not reducible and that the products do not undergo isomerization under reaction conditions.

The stereochemical results are readily explainable in terms of the mechanisms previously proposed in the literature (1-3).



III

Thus species II, a "free" radical would be expected to exist largely in the configuration in which the methyl group is in the equatorial position and hydrogen transfer from the relatively uncrowded thiol (reaction 2) would occur axially. However, reaction 3 which is obviously slower than 2, would be

expected to yield a predominant amount of the alkyl chromium derivative with the chromium in an equatorial position. With this picture, reaction 4 would be expected to proceed stereospecifically with retention of configuration.

ACKNOWLEDGMENT

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