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Dehalogenations of 2,3-Dihalobutanes by Alkali Naphthalenes. A CIDNP and Stereochemical Study

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Abstract: In reactions with alkali naphthalenes, *meso*- and *dl*-2,3-dichloro- and dibromobutanes give *cis*- and *trans*-2-butenes in over 90% yields. With sodium naphthalene in DME, *meso*- and *dl*-2,3-dichlorobutanes give 76% *trans*-2-butene (24% cis). *meso*-2,3-Dibromobutane gives 66–79% *trans*-2-butene (34–21% cis), and *dl*-2,3-dibromobutane gives 39–67% *trans*-2-butene (61–33% cis). When the reactions are carried out in magnetic fields of 60 G, the 2-butenes exhibit CIDNP. These facts are not consistent with two-electron reductive elimination pathways. They are consistent with the following one-electron pathway: RX_2 $(+NaC_{10}H_8) \rightarrow \cdot RX$ $(+NaC_{10}H_8) \rightarrow [^-:RX] \rightarrow$ 2-butene. Intermediate 2-chloro-1-methylpropyl radicals probably suffer essentially complete rotameric relaxation, thereby losing their "memories" of the diastereomers from which they were formed. Rotameric relaxation in intermediate 2-bromo-1-methylpropyl radicals may be incomplete, since *meso*- and *dl*-2,3-dibromobutanes give rise to different 2-butene mixtures. Fragmentation of 2-bromo-1-methylpropyl radicals to bromine atoms and 2-butene may account for lower CIDNP intensities from reactions of 2,3-dibromobutanes than from 2,3-dichlorobutanes. Alternatively, or in addition, an initial one-electron transfer with multiple fragmentation may occur: RX_2 $(+NaC_{10}H_8) \rightarrow$ 2-butene $+ X^- + X\cdot$. Neither of the latter two processes would give rise to CIDNP in the 2-butenes. The form of the observed CIDNP is different from that previously observed for reactions of sodium naphthalene with alkyl halides in low magnetic fields, but it appears that the accepted radical pair CIDNP model can accommodate this.

Sodium naphthalene reacts with vicinal dihalides to give olefins in yields better than 90% even in cases where many conventional reagents fail.[1] Since sodium naphthalene reacts with simple alkyl halides through an initial dissociative electron transfer (eq 1),[2] it seemed likely, a priori, that

$$RX + NaC_{10}H_8 \longrightarrow R\cdot + NaX + C_{10}H_8 \qquad (1)$$

intermediate alkyl radicals are involved in the dehalogenations of vicinal dihalides as well.

Two probes seemed directly and immediately applicable to this question, CIDNP[3] and stereochemistry. The applicability of CIDNP to reactions of sodium naphthalene has been demonstrated recently for reactions with alkyl halides[4] and proton sources.[5] In these cases, high-field CIDNP experiments fail, but polarization does result from appropriate reactions carried out in fields of the order of 100 G. The dehalogenations are a potentially interesting variant of the alkyl halide systems previously studied.

There has been an earlier report of the stereochemistry of dehalogenation by sodium naphthalene.[6] It was found that *erythro*- and *threo*-2,3-dibromo-3-methylpentanes react with sodium naphthalene in DME to give products of anti elimination to the extents of 76 and 92%, respectively.

We have studied reactions of the diastereomeric 2,3-dichloro- and 2,3-dibromobutanes with lithium, sodium, and cesium naphthalenes in DME at room temperature and at −78°.

Experimental Section

Alkali naphthalene solutions were prepared as previously described.[7] Concentrations were determined by quenching aliquots with water and titrating the resulting solutions with dilute hydrochloric acid.[8]

meso-2,3-Dibromobutane was prepared by the addition of bromine to *trans*-2-butene at 0° in carbon tetrachloride. It was purified by distillation on an annular Teflon spinning band column under reduced pressure; bp 55–56° (22 mm). *dl*-2,3-Dibromobutane was prepared similarly from *cis*-2-butene; bp 63° (28 mm). *meso*-2,3-Dichlorobutane and *dl*-2,3-dichlorobutane were similarly prepared from *trans*- and *cis*-2-butenes and chlorine in carbon

tetrachloride at 0°: meso, bp 113° (760 mm); *dl*, bp 117° (760 mm).

The purity of all the dihalides was greater than 99% as determined by VPC using a 14 ft × ⅛ in. 35% poly(phenyl ether) on Chromosorb W column at 150°.

cis- and *trans*-2-butenes were determined by VPC on a 20 ft × ⅛ in. Porapak S column at 130°, using a digital integrator and an internal standard (hexane).

In CIDNP experiments a radical anion solution (0.5 ml) was injected into an evacuated NMR tube sealed with a serum cap. A twofold excess of dihalide was injected with the tube held so that the two reagents did not mix. The solutions were mixed vigorously by shaking in the selected magnetic field until the color of the radical anion disappeared (ca. 2 sec). The tube was transferred rapidly to the spectrometer and a selected segment of the NMR spectra was determined by rapid scanning. If polarization was seen on the first scan, the region was rescanned repeatedly until spin–lattice relaxation was complete. From these data, extrapolations to zero time gave estimates of the initial signal enhancement factors.[2e]

Low magnetic fields (60 G) were provided by Helmholtz coils. High fields (5000 G) were provided by a permanent magnet. NMR spectra were recorded on a Hitachi R20 spectrometer (60 MHz).

Results

To establish whether the *cis*- and *trans*-2-butenes formed from reactions of the isomers of the 2,3-dihalides with sodium naphthalene in DME would isomerize during the process of reaction, control experiments were devised subjecting the butenes to conditions similar to that in normal reactions. Four solutions of sodium naphthalene (~0.1 *M*) were made up in evacuated Pyrex containers. In two of these solutions *trans*-2-butene was introduced through a septum with a syringe equipped with a balloon and a three-way stopcock. *cis*-2-Butene was introduced into the other two sodium naphthalene solutions in the same manner. One pair of control solutions, one containing *trans*- and the other *cis*-2-butene, was treated with 1,2-dibromethane. The remaining pair was treated with 1,2-dichloroethane. *cis*- and *trans*-2-butenes were analyzed by VPC using a 20 ft × ⅛ in. Porapak S column at 130°. No isomerization of the butenes was detected in any case.

To establish that sodium bromide formed during a reaction of sodium naphthalene with 2,3-dibromobutane does not promote the debromination of 2,3-dibromobutane, in either the room-temperature reaction mixture or in the heated injector port of the VPC instrument, the following control experiment was performed. Bromine in DME was injected in small quantities into a solution of sodium naphthalene (0.154 *M* in DME) until the green color of sodium naphthalene was almost gone. The remaining sodium naphthalene was quenched with air. About 100 μl of *dl*-2,3-dibromobutane was introduced, and samples of the mixture were analyzed for 2-butene in the usual way after 30 min and about 20 hr. In neither case was 2-butene detected.

Yields of 2-butenes were 90 to 95% in selected reactions of all the dihalides. The remaining 5 to 10% is thought to be alkylated naphthalenes.[9]

CIDNP was not found from reactions carried out at 5000 G. Reactions in fields of 0 and 60 G gave rise to polarized 2-butenes. Typical spectra for the *vic*-dichlorides are shown in Figure 1. Multiplet structure is obliterated by the rapid scanning necessary to record the polarized signals before they are destroyed by spin–lattice relaxation. Fine structure is also blurred by the superposition of the spectra of *cis*- and *trans*-2-butenes. Polarization from the 2-butenes resulting from the reactions of the dibromobutanes (Figure 2) with alkali naphthalenes is less intense by a factor of 7 to 10 than that resulting from the dichlorobutanes.

In addition to polarized butenes, CIDNP was observed at 60 G in the NMR for peaks attributed to dihydronaphthalene derivatives. The intensities of these polarized signals from the derivatives appeared to be the same regardless of the dihalide employed for reaction, Figure 3. Initially it was felt that the CIDNP in Figure 3 might result from an alkyl dihydronaphthalene anion intermediate, but this idea was discarded after observing that the anion of dihydronaphthalene (Figure 4) gave rise to one set of peaks in the aromatic region of the NMR. Figure 3 clearly indicates two sets of peaks closely corresponding with those observed for the aromatic and olefinic protons of dihydronaphthalene, Figure 4.

The stereochemical results are gathered in Tables I and II. The values tabulated are the percentages of *cis*-2-butene in the 2-butene products. It is seen that the diastereomeric 2,3-dichlorobutanes give the same, very reproducible product distribution, but that the diastereomeric 2,3-dibromobutanes give different product distributions with considerably more scatter.

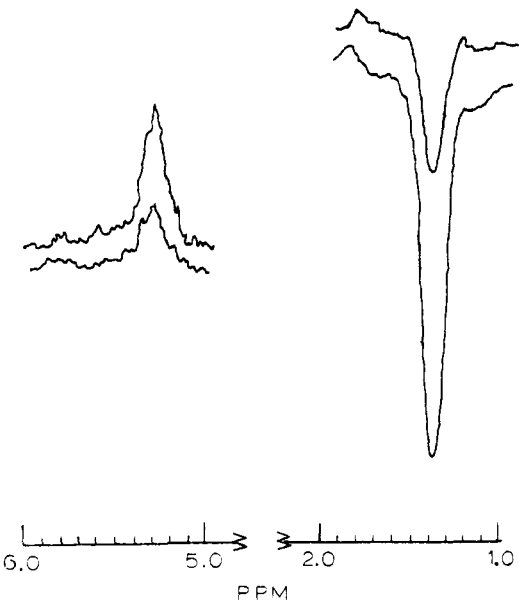


Figure 1. NMR spectra (60 MHz) of 2-butenes generated in reactions of 2,3-dichlorobutane with sodium naphthalene in DME in a field of 60 G. Left, olefinic protons; right, methyl protons. In each case the more intense signal was recorded 20 sec and the less intense signal 32 sec after the reaction was carried out. Extrapolations to time zero and comparisons with signal intensities at time infinity indicate that the original signal enhancement factors were in the range 20–50.

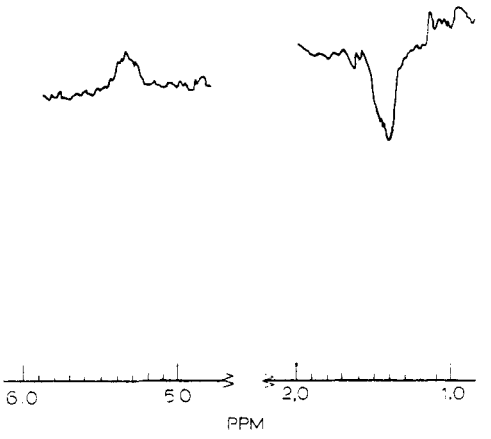


Figure 2. NMR spectra (60 MHz) of 2-butenes generated in reactions of 2,3-dibromobutane with sodium naphthalene in DME in a field of 60 G. Left, olefinic protons; right, methyl protons. Peaks recorded approximately 4 sec after reaction was carried out.

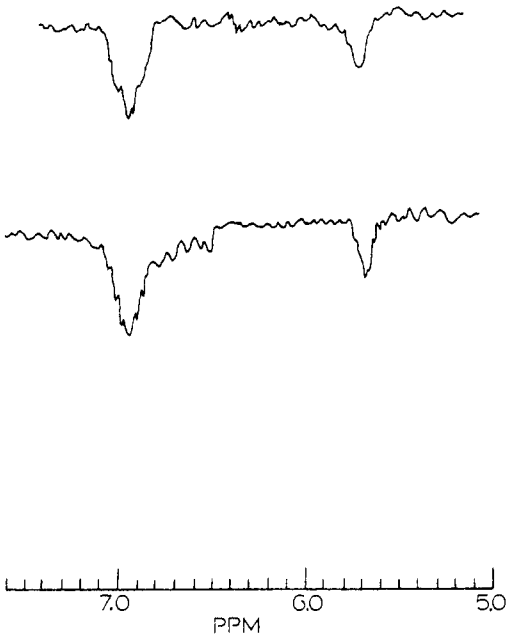


Figure 3. NMR spectra (60 MHz) of dihydronaphthalene derivatives generated in reactions of vicinal dihalides with a 0.113 *M* solution of sodium naphthalene in DME in a field of 60 G. Top spectrum, ClDNP from reaction of *meso*-2,3-dibromobutane; bottom spectrum, ClDNP from reaction of *meso*-2,3-dichlorobutane. Top left peak recorded at 4.6 sec: top right at 4.0 sec; bottom left at 4.4 sec; bottom right at 4.0 sec.

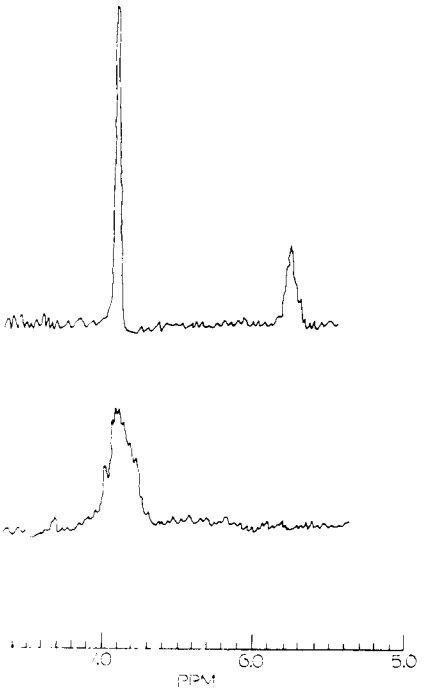
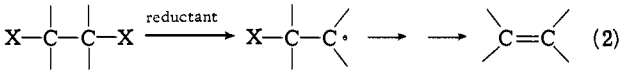


Figure 4. NMR spectra of: top peaks, 1,4-dihydronaphthalene in DME at 25° (left, aromatic proton; right, olefinic protons); bottom peak, sodium dihydronaphthalene after reaction with sodium metal in an NMR bulb tube.

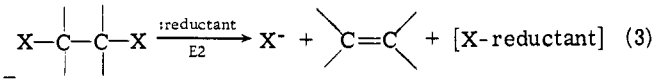
Discussion

Reductive dehalogenations of vicinal dihaloalkanes have been classified as one-electron or two-electron processes,[10] depending on the nature of the initial reaction steps and intermediates, if any. One-electron processes involve initial one-electron transfers or atom abstractions. Typically, these lead to haloalkyl radical intermediates (eq 2). Typical two-



(2)

electron processes are E2 eliminations (eq 3).



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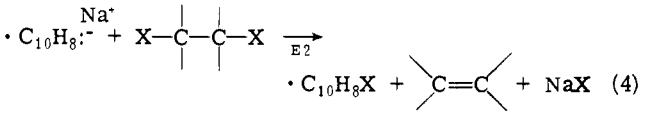
The two-electron E2 processes normally proceed with high specificity for *anti-periplanar* elimination.[10] The one-electron processes lack high stereospecificity for several possible reasons to be discussed later.

The facts that the 2-butene products of reactions of alkali naphthalenes with 2,3-dihalobutanes are stable to reaction conditions and that in no case is a high stereospecificity observed (Tables I and II) definitively rule out anti eliminations through E2 processes. Equation 4 illustrates a process,



(4)

closely related to halogen–metal interchange, perhaps, which might have occurred, but clearly does not. If these are two-electron reductive dehalogenations, they are not of the typical E2 type.

If the alkali naphthalene dehalogenations are one-electron processes, the stereochemistry might resemble closely those which have been found for other one-electron reductants. In Table III, two well-established one-electron reductants, tributyltin hydride[11] and chromium(II),[12] are compared with sodium naphthalene with respect to stereochemistries of dehalogenations of 2,3-dihalobutanes. The correspondence is excellent.

All three reagents are stereoselective in their reactions with the 2,3-dichlorobutanes, giving 70–83% *trans*-2-butene from both meso and *dl* substrates. Within experimental error, the product distributions are identical from the two diastereomeric substrates.

With the 2,3-dibromobutanes, meso and *dl* isomers give different mixtures of 2-butenes from reactions with each of the three reagents. Tributyltin hydride dehalogenations are slightly stereospecific for anti elimination,[13] while both chromium(II)[14] and sodium naphthalene give rather evenly balanced mixtures of 2-butenes, especially from *dl*-2,3-dibromobutane.

These similarities are certainly consistent with one-electron reductive dehalogenations by sodium naphthalene, but they do not demand this theory. In fact, the reactions of sodium naphthalene, chromium(II), and tributyltin hydride are all complicated by various theoretical and experimental factors which keep them from being really directly comparable. The tributyltin hydride experiments, for example, were hampered by instability of the product olefins under reaction conditions.[12] The chromium(II) reactions are believed to involve haloalkylchromium species whose decomposition may involve syn or anti eliminations to the final olefinic products, depending on conditions.[11] And it is quite conceivable that corresponding haloalkylsodium intermediates may be involved in the sodium naphthalene reactions. Thus, the factors affecting stereochemistry may be quite varied among dehalogenations by these three reagents, and some of these factors may have nothing to do with whether the processes are one-electron or two-electron reductions.

In the cases of tributyltin hydride and chromium(II), substantial evidence other than stereochemistry was obtained in support of one-electron dehalogenation mechanisms.[11,12] The same lines of evidence are not available for

Table I. Distribution of 2-Butenes from Reactions of Alkali Naphthalenes with 2,3-Dichlorobutanes in DME at Room Temperature

Diastereomer	Alkali metal	$[MC_{10}H_8]_0$[a]	*cis*-2-Butene[b]
Meso	Li	0.0030	25
		0.014	25
		0.051	25
		(0.051)[c]	(27)[c]
		0.003 (−78°)	28
	Na	0.0075	22
		0.068	23
		0.13	23
		(0.0075)	(24)
		(0.068	(25)
		(0.13)	(24)
dl	Li	0.0014	26
		0.051	25
		(0.051)	(21)
		0.051 (−78°)	26
	Na	0.0075	23
		0.068	24
		0.13	22
		(0.0075)	(25)
		(0.13)	(25)
		0.068 (−78°)	25

[a] Initial concentration of alkali naphthalene in moles/liter. [b] Percentage of the 2-butenes. [c] Excess dihalide injected for experiments with results in parentheses. Otherwise alkali naphthalene was in excess.

Table II. Distribution of 2-Butenes from Reactions of Alkali Naphthalenes with 2,3-Dibromobutanes in DME at Room Temperature

Diastereomer	Alkali metal	$[MC_{10}H_8]_0$[a]	*cis*-2-Butene[b]
Meso	Li	0.0011	17
		0.0014	14
		0.046	20
		0.051	22
		(0.046)[c]	(21)[c]
		(0.051)	(25)
	Na	0.0025	25
		0.0075	27
		0.068	27
		0.13	21
		(0.0075)	(34)
		(0.068)	(27)
		(0.13)	(24)
		(0.015) (−78°)	10
	Cs	0.042	25
		(0.042) (−78°)	(17)
dl	Li	0.0011	61
		0.046	48
		0.155	51
		(0.0011)	(69)
		(0.003)	(67)
		(0.046)	(55)
		(0.155)	(55)
		0.0105 (−78°)	45
	Na	0.0025	39
		0.0075	46
		0.068	33
		0.13	38
		(0.0075)	(61)
		(0.068)	(47)
		(0.13)	(52)
		(0.0025((−78°)	(42)
	Cs	0.010	57
		0.010	59

[a] Initial concentration of alkali naphthalene in moles/liter. [b] Percentage of the 2-butenes. [b] Excess dihalide injected for experiments with results in parentheses. Otherwise alkali naphthalene was in excess.

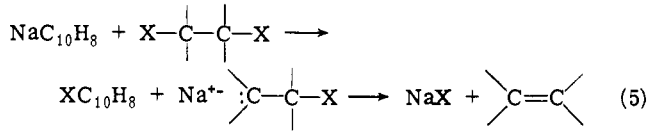
Table III. Relative Yields of *cis*-2-Butene from Reactions of 2,3-Dihalobutanes with Tributyltin Hydride, Chromium(II), and Sodium Naphthalene[a]

Compd	Bu_3SnH[b]	Cr(II)[c]	$NaC_{10}H_8$
meso-2,3-Dichlorobutane	17	30	22–25
dl-2,3-Dichlorobutane	23	30	22–25
meso-2,3-Dibromobutane	10–16	21–27	21–27[d]
dl-2,3-Dibromobutane	59–80	39–53	33–46[e]

[a] Values tabulated are the percentages of the 2-butenes which are cis. [b] From ref 12. [c] From ref 11c. The experiments summarized here are for acidic chromium(II) solutions in ethanol and DMF and for chromium(II)–ethylenediamine in DMF. In DMSO there was a moderately high stereospecificity for anti elimination. [d] For experiments with excess sodium naphthalene. With excess *meso*-2,3-dibromobutane a value of 34 was found in one experiment. [e] For experiments with excess sodium naphthalene. With excess *dl*-2,3-dibromobutane values ranged from 42 to 57.

reactions of sodium naphthalene, but another kind of evidence is, that from CIDNP.[2e,3-5]

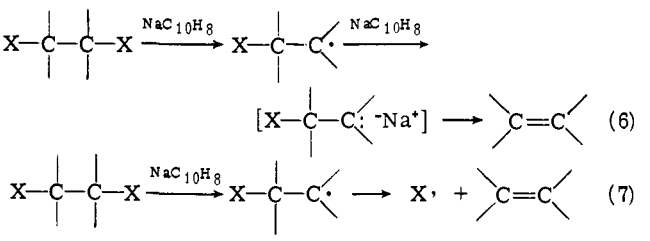
Five fundamental requirements of CIDNP are pertinent: (1) there must be a free-radical precursor of the product in which CIDNP is observed; (2) there must be magnetic nuclei in that free radical (for chemically induced proton polarization, protons, of course, are required); (3) at least one of the magnetic nuclei must have a significant isotropic coupling constant with the odd electron; (4) at least one of the electron-coupled nuclei must be carried into the product molecule; and (5) there must be some radical–radical reaction of the free-radical precursor.[2e,3] Two-electron reductive dehalogenations do not meet these requirements for CIDNP in the olefin products. Consider eq 4 augmented by a subsequent radical–radical reaction between $NaC_{10}H_8$ and $C_{10}H_8X$. This mechanism meets requirements 1–3 with $NaC_{10}H_8$ and requirement 5 with the radical–radical reaction just mentioned. However, it does not meet requirement 4, and therefore it is a non-CIDNP mechanism for the olefin products. Equation 5 represents another conceivable



(5)

two-electron process, one in which halogen–metal interchange precedes loss of X^- from the dihaloalkane. Again, $XC_{10}H_8$ is presumed to react with $NaC_{10}H_8$ to generate naphthalene and sodium halide. Again, the mechanism meets requirements 1–3 and 5, but not requirement 4, and therefore this mechanism is also a non-CIDNP process for olefins.

One-electron reductive dehalogenations may or may not meet the requirements for olefin CIDNP, depending on the details. Consider processes 6–8. Equation 6 represents a CIDNP pathway for olefins, since it satisfies all five requirements listed above. The radical–radical step is the reaction of the haloalkyl radical with sodium naphthalene, and the protons carried forward into the product are those of the dihaloalkane substrate. The mechanism of eq 7 is a



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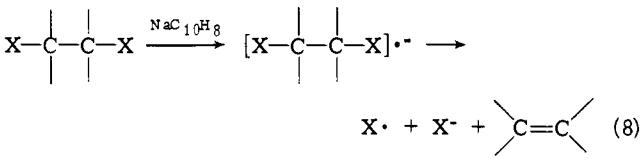
(7)

non-CIDNP process for the olefin products because there is no radical–radical reaction of the haloalkyl radical intermediate. For the same reason, the mechanism of eq 8 is a non-



CIDNP process for olefin formation. Thus, one-electron reductive dehalogenations by sodium naphthalene may or may not give CIDNP in the olefin product.

In fact, CIDNP is found in the olefin products, provided that the reactions are carried out in low magnetic fields (Figures 1 and 2). The requirement for low fields has been rationalized previously for processes analogous with eq 6.[2e,4b] This is additional direct support for the one-electron process of eq 6, which is analogous with the mechanisms proposed for reductive eliminations of halogens by chromium(II) and tributyltin hydride.[11,12]

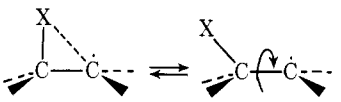
For reactions of 2,3-dichlorobutanes, extrapolations of signal intensities to time zero (on first-order plots) give values corresponding to initial signal enhancement factors in the range 20–50. These compare favorably with those (ca. 20) found for reactions of simple alkyl halides with sodium naphthalene in DME,[2e] reactions which proceed entirely through alkyl radical–sodium naphthalene reaction steps. This is semiquantitative support for the idea that eq 6 describes the *exclusive* pathway for the 2,3-dichlorobutanes.

The olefins from reactions of 2,3-dibromobutanes are polarized to an extent that is 7–10 times less than from the 2,3-dichlorobutanes. The observation of CIDNP at all supports the mechanism of eq 6, but the semiquantitative argument for exclusiveness used above is not applicable. It is difficult to attribute the lower polarization from the dibromoalkanes to a particular factor; there are a number of possibilities. Two of the more likely seem to be halogen-dependent spin or spin-coupling effects in the haloalkyl radicals, perhaps due to bridging in the bromoalkyl radicals,[15] and the incursion of non-CIDNP pathways such as those represented by eq 7 and 8.

We are left with the conclusions that stereochemistry rules out conventional two-electron E2 processes, stereochemistry is in a general way consistent with one-electron processes, and CIDNP actively supports the one-electron process of eq 6 for reactions of sodium naphthalene with 2,3-dihalobutanes in DME. We return again to considerations of the stereochemistry with reaction 6 as the mechanistic basis.

In reactions like 2 and 6, three factors may be responsible for a lack of high stereospecificity: (1) the initial step may be nonstereospecific or only partly stereospecific; (2) rotameric relaxation may occur in the intermediate haloalkyl radicals, completely or partially destroying any stereochemical integrity with which they might have been formed; and (3) some process in an intermediate *subsequent to* the haloalkyl radicals may be deficient in stereochemical integrity. For reaction 6, the process of factor 3 would be the rotameric relaxation preceding loss of halide ion from the haloalkyl anions.

Assuming that *meso*- and *dl*-dichlorobutanes do not give rise fortuitously to the same initial distributions of rotamers of 2-chloro-1-methylpropyl radicals, the finding of the same ultimate distributions of isomeric 2-butenes implies essentially complete rotameric relaxation in the 2-chloro-1-methylpropyl radicals or, in the case of reaction 6, in the 2-chloro-1-methylpropyl anions. A lower limit on the rotameric relaxation in the chloroalkyl radicals can be set by assuming that they are bridged and that opening to an unbridged radical (eq 9) is the slow step in rotameric relaxation. Skell has estimated the rate constant for opening of a related chloroalkyl radical as 4.5×10^9 sec^{-1}.[15] Since the mean lifetime of intermediate alkyl radicals in reactions of alkyl halides with sodium naphthalene is about 0.5×10^{-8} sec in a 0.1 *M* sodium naphthalene solution,[16] it is predicted that intermediate chloroalkyl radicals should suffer essentially complete rotameric relaxation in sodium naphthalene solutions. A similar prediction applies to tributyltin hydride and chromium(II) solutions, and the similar and consistent findings for all three reductants (Table III) are in agreement with these predictions.



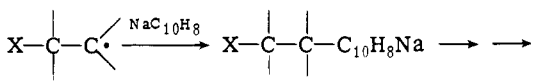
For dehalogenations of 2,3-dibromobutanes, the situation is much more complex. If eq 6 represents the exclusive pathway to olefins, rotameric relaxation cannot be complete in either intermediate 2-bromo-1-methylpropyl radicals or possible intermediate 2-bromo-1-methylpropyl anions, since *meso*- and *dl*-2,3-dibromobutanes give rise to different distributions of *cis*- and *trans*-2-butenes. If there is a significant competition between rotameric relaxation in intermediate 2-bromo-1-methylpropyl radicals and reactions of these radicals with alkali naphthalenes, there should be a concentration (of alkali naphthalene) effect on the product distribution. Such an effect is not evident in the data, although the scatter could obscure small trends, and some series do seem to show trends. The scatter itself could be taken as evidence for a concentration effect. The high precision of the analytical data in Table I indicates that the scatter is probably not due to analytical procedures. It could be due to the fact that these are very fast reactions which occur while the reagents are being mixed. Under such conditions, local concentrations may be unknowable and unreproducible. It is tempting to attribute the scatter to concentration effects acting in this fashion, but the only substantial conclusion the data allow is that concentration effects, if there are any, are small. It should be noted that a similar conclusion describes corresponding data for reactions of 2,3-dibromobutanes with chromium(II) and tributyltin hydride.[11c,12]

Analogy with reactions of chromium(II) suggests that process 7, involving the spontaneous loss of Br· from bromoalkyl radicals, may be competitive with reaction 6. Singleton and Kochi found evidence for the analogous competition in reactions of several *vic*-dihaloalkanes with 0.05 *M* chromium(II).[11b] Kochi several times expressed the opinion that reactions of alkyl radicals with chromium(II) should be close to diffusion controlled,[11b,c] and by competitive experiments using 6-bromo-1-hexene (a precursor of the 5-hexenyl radical, which undergoes a facile cyclization) Kochi and Powers established the rate constant for the reaction of 5-hexenyl radicals with chromium(II) ethylenediamine at 25° as 4×10^7 M^{-1} sec^{-1}.[18] Thus, at 0.05 *M* chromium(II), the pseudo-first-order rate constant for reactions of alkyl radicals with chromium(II) is estimated as 2×10^6 sec^{-1}. Similarly, Garst and Barton found the rate constant for the reaction of 5-hexenyl radicals with sodium naphthalene to be 2×10^9 *M* sec^{-1}.[17] At 0.0025 *M* sodium naphthalene (the lowest concentration in Table II), this corresponds to a pseudo-first-order rate constant for reactions of alkyl radicals with sodium naphthalene of 5×10^6 sec^{-1}, which is very similar to that in the chromium(II) solutions where fragmentation of bromoalkyl radicals is believed to be significant.

Thus, the theory which is most consistent with the facts cited above is that eq 6 describes the reactions of 2,3-dichlo-

robutanes with sodium naphthalene, but that eq 6 and 7 describe the similar reactions of 2,3-dibromobutanes. If the loss of Br· from 2-bromo-1-methylpropyl radicals is competitive with or faster than rotameric relaxation, which may be hindered by bromine bridging (eq 9),[15] then the different distributions of *cis*- and *trans*-2-butenes from *meso*- and *dl*-2,3-dibromobutanes are accounted for. The same theory accounts for the attenuated CIDNP in the 2-butenes from reactions of 2,3-dibromobutanes, compared with reactions of 2,3-dichlorobutanes, since 6 is a CIDNP process but 7 is non-CIDNP. By supposing that the extent of rotameric relaxation in 2-bromo-1-methylpropyl radicals is small in these reactions, the small effect of the concentration of lithium and sodium naphthalenes is accounted for. The variations in stereochemistry which are found must then be attributed mainly to variations in the initial reaction step or in rotameric relaxation in possible 2-bromo-1-methylpropyl anions.

One piece of weak evidence is not in good accord with this picture. The evidence concerns the CIDNP from products assumed to be derivatives of dihydronaphthalenes. Reaction 6 allows for the formation of such derivatives through coupling of haloalkyl radicals with sodium naphthalene (eq 10), which can compete with electron transfer



substituted dihydronaphthalenes (10)

and does so compete in reactions of monohaloalkanes with sodium naphthalene.[2d,e] Since radical coupling is involved, this is a CIDNP pathway. Reaction 7 makes no provision for the formation of dihydronaphthalene derivatives. Thus, if reaction 7 competes with reaction 6, the yields of dihydronaphthalene derivatives should thereby be diminished. In fact, the intensities of CIDNP in the dihydronaphthalene derivatives are similar from reactions of 2,3-dichlorobutanes and 2,3-dibromobutanes (Figure 3), suggesting that the yields of these products are similar. Similar yields would be difficult to reconcile with significant incursion of reaction 7 for 2,3-dibromobutane reactions but not for 2,3-dichlorobutane.

On the basis of the present data, we cannot speak of the probability that process 8 is occurring instead of, or in addition to, reactions 7. It is reasonable to speculate that reaction 8 would be a preferential *anti-periplanar* process, since this would meet the stereoelectronic requirements for the developing olefinic double bond while avoiding the steric difficulties of a *syn-periplanar* process. Because anti elimination is not the exclusive process and because CIDNP is observed (reaction 8 is a non-CIDNP process), reaction 8 cannot be the exclusive mechanism of the reaction. If reaction 8 contributes at all, it is reasonable to suppose that it may occur in those instances in which the alkali naphthalene reacts directly with an anti-periplanar conformer, and that the normal initial step of reactions 6 and 7 occurs otherwise. It is possible that reaction 8 occurs in the exclusively anti electrochemical debrominations of *vic*-dibromoalkanes at stirred mercury cathodes at low potentials and currents.[19] As noted by Kochi and Singleton,[11c] a process analogous with reaction 8 could also account for rate accelerations in reactions of *vic*-dibromoalkanes with chromium(II); conventionally, these accelerations are attributed instead to bromine bridging during the formation of an intermediate bromoalkyl radical (eq 2).[11]

There is no requirement for the carbanion intermediate shown in eq 6. The transfer of the second electron and the loss of the second X^- could be synchronous.

While there are ample opportunities in reactions 6–8 for metal ion effects, those which were observed are quite small, too small to justify attempts at their interpretation.

The moderate stereospecificities for anti elimination in reactions of 2,3-dibromo-3-methylpentanes are also consistent with reactions 6 and 7, but not consistent with two-electron E2 processes.[6] The differences between that system and the 2,3-dibromobutanes do not constitute a conflict, since differing conformational and steric factors in the two systems could easily account for the differences in stereochemical patterns. However, there is some semantic confusion in the paper of Adam and Arce[6] which should be cleared up. They state their conclusion, "that the reaction of . . . [*erythro*- and *threo*-2,3-dibromo-3-methylpentanes] . . . with sodium naphthalenide is a two-electron trans elimination",[6,20] then they write eq 6 as their proposed mechanism. Clearly, there is no conflict between their basic interpretation and ours, but we consider that their usage of "two-electron" differs from that of the prior literature.[10]

Finally, we note that one-electron mechanisms of dehalogenation of *vic*-dihaloalkanes by alkali naphthalenes, chromium(II), and tributyltin hydride are supported by analogies with corresponding reactions of monohaloalkanes. For each reagent, there is substantial evidence for an initial loss of X^- or X· from RX, leading to an alkyl radical in a step that is parallel to the first step of eq 2, 6, or 7.[2,21,22]

Field Dependence and Form of CIDNP. The absence of CIDNP from high-field reactions was anticipated by analogy with previous results.[4] It is attributed to suppression of spin selection by rapid retrapping of alkyl radicals which escape reaction with the sodium naphthalene ion pairs they initially engage. In essence, all initially formed intermediate alkyl radicals are rapidly scavenged by sodium naphthalene, so that there is no net spin selection and, thus, no CIDNP. A quantitative treatment of a model process has been given elsewhere.[4b,c]

There were two surprises in the CIDNP from reactions of 2,3-dihalobutanes with sodium naphthalene. First, some of the polarization is enhanced absorption. Previously, we had observed only emission in alkanes resulting from reactions of alkyl halides with sodium naphthalene. Second, polarization persists from reactions carried out in magnetic fields approaching zero. Previously, CIDNP had been found to vanish in sufficiently low fields for reactions of simple alkyl halides with sodium naphthalene.

It does not appear that either effect is inconsistent with the conventional CIDNP theory for these reactions. In the course of calculations for other purposes, the same kinds of effects (qualitatively) were found for a model system closely related to the present case. We shall describe these calculations.

Radical pairs [$YCH_2\dot{C}HZ$ R·] were considered, where Y, Z, and R are groups without nuclear spins. YCH_2CHZ is considered analogous with $CH_3\dot{C}HCHXCH_3$ and R· represents $NaC_{10}H_8$. Radical pair dynamics were treated according to a density matrix formulation of the CKO model,[23] with modifications to be described. We no longer use this model, having abandoned it in favor of a diffusional model,[24] but the qualitative effects should be similar for both models. A uniform density matrix was taken to describe the initial nuclear spin distribution of the first generation of radical pairs [$YCH_2\dot{C}HZ$ R·].[25] Radicals $YCH_2\dot{C}HZ$ calculated to escape reactions with their partners in the first generation of radical pairs were considered to be trapped immediately by engaging another R· to form a second generation of radical pairs. The nuclear spin density matrix θ for radicals escaping the first generation pairs was taken as the initial nuclear spin density matrix for the

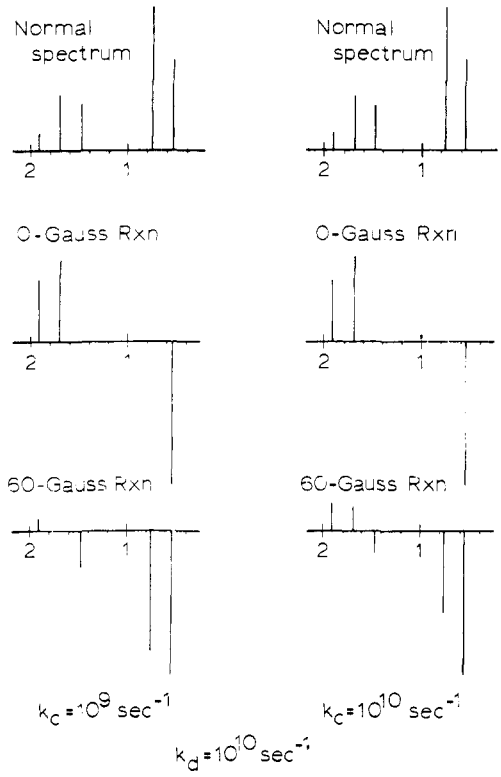


Figure 5. Calculated spectra of YCH_2CHZR. The two top spectra are the normal equilibrium spectra taking $\delta(CH_2) = 0.83$ ppm, $\delta(CH) = 1.33$ ppm, and $J(CH_2\text{-}CH) = 7$ Hz, values which might be appropriate for an ethyl group (CH_2 analogous with CH_3; CH analogous with CH_2). In the calculations for reactions in fields of 0 and 60 G, the product was considered to be formed in the radical pair collapse of [$YCH_2\dot{C}HZ$ R·] with immediate retrapping of escaping radicals $Y\dot{C}H_2CHZ$, as described in the text. The nuclear-electron coupling constants were $A(CH_2) = +27$ G and $A(CH) = -22$ G, typical values for alkyl radicals. J_{eff} (the effective value of the electronic exchange coupling) was set at -2×10^8 rad/sec. The radical g values were 2.00275 and 2.00260, typical for naphthalene radical anion and alkyl radicals; however, for low-field calculations the g values have essentially no effect on the results. The rate constant for diffusive separation was set at 10^{10} sec^{-1} and that for radical pair collapse was taken as 10^9 and 10^{10} sec^{-1}. The intensities of plotted signals are correct within each spectrum, but the spectra are normalized so that the most intense peak is the same height (or depth) in all spectra. The figures on the horizontal axes are chemical shifts (δ) in ppm.

second generation of radical pairs. This process was repeated until negligible amounts of the radicals $YCH_2\dot{C}HZ$ were computed to remain unreacted. The product nuclear spin density matrix, from which the NMR spectra were calculated, was taken to be the sum of the density matrices γ (appropriately normalized) for the products of collapse of the various generations of radical pairs. Populations of nuclear spin states in the high field of a 60 MHz NMR spectrometer were calculated assuming adiabatic transfer from the low fields of reactions, as usual.[3]

In the CKO model radical pairs vanish in first-order processes with a net time constant τ. Equation 11 gives the

$$\gamma = k_c \int_0^\infty s(t) e^{-t/\tau} dt \qquad (11)$$

probability γ that a radical pair formed at time zero will ultimately collapse to product rather than diffuse apart. In eq 11 $s(t)$ is the (time dependent) electronic singlet character and k_c is the first-order rate constant for collapse of pure electronic singlet radical pairs. The modified model with which the present calculations were done simply takes τ to be a function of two first-order rate constants, k_c and k_d (describing diffusive radical pair separation) (eq 12). In

$$1/\tau = k_d + \sigma k_c$$
$$\sigma = 0 \text{ for T pairs; } \sigma = 1 \text{ for S pairs} \qquad (12)$$

eq 12, σ is the initial electronic singlet character of the radical pair. Our calculations involve random spin pairs formed by the diffusion together of independently generated radicals. These are initially described by uniform electronic spin density matrices, which, in these calculations, is equivalent to considering them as ¼ electronic singlet radical pairs (S pairs) and ¾ triplet pairs (T pairs), the latter being evenly divided among the three components.

The spectra plotted in Figure 5 illustrate the effects of radical pair reactivity. The parameters for this calculation were chosen to represent an alkyl radical $YCH_2\dot{C}HZ$ and a typical alkane product YCH_2CHZR (see legend for Figure 5). Two reaction fields are represented, 0 and 60 G, and the stick spectra are compared with the normal spectrum of the product (at equilibrium). (At high fields the calculated CIDNP intensities fall to insignificant levels, as they should.)[4b] The plotted spectra have been scaled for convenience of comparisons; the apparent intensity of the strongest peak (positive or negative) is the same for all.

For the 60-G reactions, the form of the CIDNP spectrum is sensitive to the radical pair reactivity. When k_c is chosen as 10^9 sec^{-1} (representing 9% cage reaction) emission is dominant from both sets of product protons. This is the kind of observation we have made previously for a variety of reactions of simply alkyl halides with sodium naphthalene. When k_c is increased to 10^{10} sec^{-1} (representing 50% cage reaction), the CH_2 group is still emissive, but the CH group appears mostly in enhanced absorption. This is the kind of observation we have made for reactions of 2,3-dihalobutanes with sodium naphthalene. Since our scan rate is necessarily too fast to resolve fine structure, we must assume that we will record only the dominant effect (absorption or emission) for closely spaced lines. Thus, the calculations are consistent with the data provided that it is assumed that radicals $CH_3\dot{C}HCHXCH_3$ are somewhat more reactive toward sodium naphthalene than simple alkyl radicals; this is certainly not unreasonable in view of the extra electronegative atom of the former radicals. It should be understood that there can be a wide spectrum of values of k_c which correspond to diffusion-controlled or nearly diffusion-controlled reactions, so that these considerations are not inconsistent with our previous estimate of the rate constant of 2×10^9 M^{-1} sec^{-1} for the reaction of the 5-hexenyl radical with sodium naphthalene in DME.[17]

In a reaction field of 0 G, the calculated spectra exhibit the typical missing center lines form that is the zero-field analog of a high-field multiplet effect. We cannot resolve the multiplets, but the general pattern (CH_2 emissive, CH absorptive) is that which is observed in the 2-butenes from reactions of 2,3-dihalobutanes with sodium naphthalene.

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Hydroboration. XXXIX. 1,3,2-Benzodioxaborole (Catecholborane) as a New Hydroboration Reagent for Alkenes and Alkynes. A General Synthesis of Alkane- and Alkeneboronic Acids and Esters via Hydroboration. Directive Effects in the Hydroboration of Alkenes and Alkynes with Catecholborane

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Abstract: Catecholborane (1,3,2-benzodioxaborole), readily available from the reaction of catechol with borane in THF, reacts rapidly with alkenes and alkynes at 100 and 70°, respectively, to give the corresponding alkyl- and alkenylcatecholboranes in high yield. These hydroborations proceed stereospecifically in a cis manner. Greater regioselectivity is realized in comparison with such hydroborations with diborane itself. The alkyl- and alkenylcatecholboranes undergo rapid hydrolysis with water to give the corresponding alkane- and alkeneboronic acids. The alkenylcatecholboranes (2-alkenyl-1,3,2-benzodioxaboroles) undergo ready protonolysis with acetic acid to give the corresponding alkenes in essentially quantitative yield. The alkaline hydrogen peroxide oxidation of alkyl- and alkenylcatecholboranes give the corresponding oxygenated products in high yield.

Alkane- and alkeneboronic acids and esters are becoming of increasing significance as intermediates in organic synthesis. For example, the *B*-alkylcatecholboranes [2-alkyl-1,3,2-benzodioxaboroles (**2**)] are converted by lithium aluminum hydride ($LiAlH_4$) or aluminum hydride (AlH_3) to the corresponding monoalkylboranes (RBH_2) in essentially quantitative yield.[2] The reaction of Grignard reagents with **2** provides a route to mixed trialkylboranes.[3] The reaction of 2-alkenyl-1,3,2-benzodioxaboroles (**3**) with mercuric acetate provides an entry to alkenylmercuric salts;[4] the latter derivatives have been used for the introduction of the prostaglandin side chain.[5] Alkeneboronic acids have been transformed to the corresponding *trans*-1-alkenyl iodides[6] (with retention) and *cis*-1-alkenyl bromides[7] (with inversion). Attention is also called to the fascinating chemistry of alkeneboronic esters, as studied extensively by Matteson and his coworkers.[8]

These developments suggested the desirability of a search for a simple, straightforward synthesis of alkane- and alkeneboronic esters. In the past, the main reliance has been organometallics. Thus, many different organometallic reagents have been reacted with various borate esters to provide simple, functionally unsubstituted alkane- and alkeneboronic esters.[8,9] Unfortunately, the yields are often low, and the procedure cannot tolerate the presence of many functional groups. A potentially more convenient and general approach, that involving the hydroboration of alkenes and alkynes with a disubstituted borane, such as 4,4,6-trimethyl-1,3,2-dioxaborinane, has been studied by Woods and Strong.[10] This reagent, however, proved to be a poor hydroborating agent.[11]

We have discovered that catecholborane (1,3,2-benzodioxaborole), readily available by the reaction of catechol with borane in THF, hydroborates representative alkenes[12]