

Reactions of 1,6-Dihalohexanes with Alkali Naphthalenes. The Radical Anion 1,6-Hexylide. Counterion Control of Multiple Reduction¹

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Abstract: Unlike 1,4-dihalobutanes and 1,5-dihalopentanes, 1,6-dihalohexanes react with lithium and sodium naphthalenes in DME to give significant amounts of dimeric (C₁₂) hydrocarbon reduction products. In addition, the monomeric four-electron reduction product (hexane) is formed, along with monomeric two-electron reduction products (cyclohexane and 1-hexene). The evidence indicates that at least part of the hexane arises through the radical anion $\cdot\text{CH}_2(\text{CH}_2)_4\text{CH}_2\cdot^-$ (1,6-hexylide), a novel species. In reactions of lithium naphthalene with 1,6-dichlorohexane, hexane is the dominant reduction product, while in the similar reactions of sodium naphthalene, cyclohexane and 1-hexene predominate. This can be understood in terms of metal ion effects on competitive reactions of 6-chlorohexylalkali intermediates.

Alkali naphthalenes (MC₁₀H₈) in ethers undergo rather clean reactions with 1,4-dihalobutanes and 1,5-dihalopentanes in that no products contain dimeric or polymeric residues of the reactant alkyl halides.²⁻⁴ Instead, the alkyl halides consumed are accounted for quantitatively by cycloalkanes, olefins, and products in which the naphthalene is monoalkylated; in some cases very small quantities of linear saturated alkanes are also formed. Since moniodoalkanes lead to alkyl dimers,^{5,6} it is evident that as the carbon chains of α,ω -dihaloalkanes are lengthened, intermolecular coupling must (at some stage) cease to be excluded by intramolecular coupling (cycloalkane formation) and olefin formation. We find, in fact, that this occurs with 1,6-diiodohexane.

In both a mechanistic and a practical sense, this complicates the reactions considerably, compared to those of 1,4-dihalobutanes and 1,5-dihalopentanes. At the same time, some potentially interesting new competitive reactions become available. Accordingly we have examined reactions of lithium and sodium naphthalenes with 1,6-diiodo-, and 1,6-dibromo-, and 1,6-dichlorohexanes in DME. The data reveal an interesting and potentially useful kind of effect, counterion control of the extent of reduction. Concomitantly, they provide evidence for a novel intermediate, the radical anion 1,6-hexylide ($\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot^-$). α,ω -Alkylides possess structural capabilities for through-bond (and through-space) interactions of the terminal functional groups. These radical anions are, of course, formal one-electron reduction products of diradicals for which such effects are of great current interest.⁷

Experimental Section

The procedures were described in detail previously.⁴ Alkyl halides were obtained commercially and purified. Unless other-

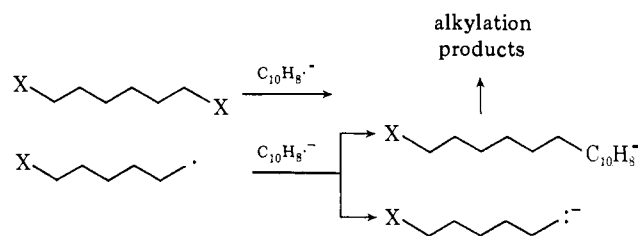
wise noted, alkali naphthalenes were in excess ($\sim 10^{-1}$ M initially). The initial concentrations of alkyl halides were about 2×10^{-2} M. Analyses were quantified by vpc using hydrocarbon internal standards.

Results and Discussion

The principle results are given in Table I and its footnotes. Other experiments will be described at relevant points.

The outstanding features of the results, compared to those for 1,4-dihalobutanes and 1,5-dihalopentanes,²⁻⁴ are the formation of dimeric (C₁₂) hydrocarbons and of large quantities of monomeric four-electron reduction product (hexane). The C₁₂ hydrocarbons are most important for 1,6-diiodohexane, and hexane is most important for lithium naphthalene and 1,6-dichlorohexane. The initial steps of the reactions can be assumed to be parallel to those proposed for similar reactions of 1,4-dihalobutanes and 1,5-dihalopentanes.²⁻⁴ These lead to 6-haloalkylalkalies and precursors of alkylation products (Scheme Ia). Four of

Scheme Ia



the reasonable fates for an intermediate 6-haloalkylalkali are detailed in Scheme Ib: reaction 1, intramolecular reaction to give cyclohexane or 1-hexene; reaction 2, reaction with 1,6-dihalohexane to give a 1,12-dihalododecane, which goes on to C₁₂ hydrocarbons (and alkylation products);⁸ reaction 3, reaction with solvent to give a 1-haloalkane, eventually giving hexane (and alkylation products); and reaction 4, reaction with alkali naphthalene to give an alkali 1,6-hexylide, which is then further reduced, eventually giving hexane.

(8) The reaction of a 6-haloalkylalkali with a 1,6-dihalohexane may also be expected to give small amounts of 1-haloalkane and 5-hexenyl halide by an elimination process.

(1) Based on the Ph.D. Dissertation of John T. Barbas, The University of Georgia, Athens, 1971.

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(3) J. F. Garst and J. T. Barbas, *Tetrahedron Lett.*, 3125 (1969).

(4) J. F. Garst and J. T. Barbas, *J. Amer. Chem. Soc.*, **96**, 3239 (1974).

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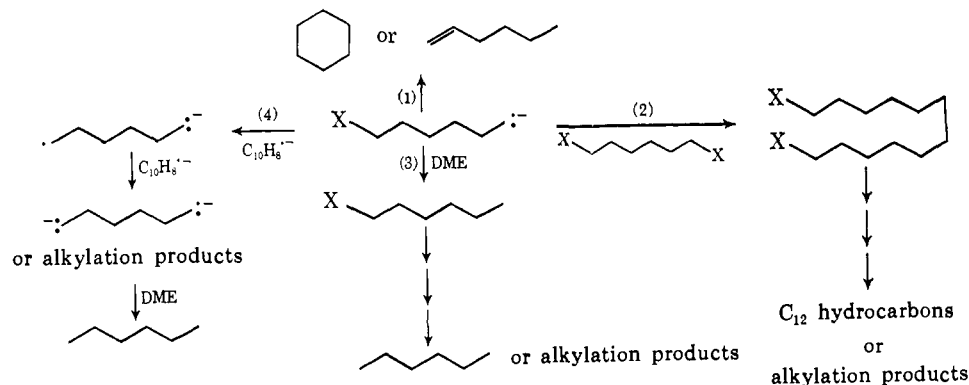
(6) G. D. Sargent and G. A. Lux, *J. Amer. Chem. Soc.*, **90**, 7160 (1968).

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Table I. Products of Reactions of 1,6-Dihalohehexanes with Alkali Naphthalenes in DME^a

M ⁺	X	Cyclohexane	1-Hexene	Hexane	Dodecane	1-Dodecene	Cyclo-dodecane
Na ⁺	I ^b	15 ± 2 (7)	19 ± 3 (7)	3 ± 1 (7)	7 (2)	9 (2)	1.6 (2)
Na ⁺	Br	26 (2)	8 (2)	3 (2)	7	3	~0
Na ⁺	Cl	10 (2)	21 ± 1 (2)	10 (2)	4	<1	~0
Li ⁺	I	21 ± 1 (4)	11 (4)	5 ± 1 (4)	9	8	1
Li ⁺	Br	18 (2)	8 (2)	24 (2)	ND ^c	ND	ND
Li ⁺	Cl	4 ± 2 (5)	1 (5)	40 ± 2 (5)	ND ^c	ND	ND

^a Yields are the percentages of the alkyl halides consumed in forming the products in question. Limits are the limits of variation for the number of experiments shown in parentheses. In each case the alkyl halide was injected into a sodium naphthalene solution with vigorous shaking. The initial concentrations of sodium naphthalene were $\sim 10^{-1} M$ while those of the alkyl halides were $\sim 2 \times 10^{-2} M$. ^b In one run the alkylation products were examined by vpc. Monoalkylation products were formed in 46% yield and the products determined accounted for 95% of the reactant 1,6-diodohexane. Two small peaks were probably dialkylation or dodecylation products. ^c Not determined. However, in these cases the total dimer yield was very small, less than 5%.

Scheme Ib

These are not all the possible processes, merely a selection of those which seem most likely to be significant.⁹ With reactions of such complexity, with several possible routes to some products, it would be futile to attempt to interpret each product yield in terms of mechanistic details. However, the gross features are subject to some testing, and the possibility that the reactions proceed through 1,6-hexylidene is sufficiently interesting to justify an attempt to substantiate it. In addition, the metal ion effect on the relative amounts of two-electron and four-electron reduction to monomeric hydrocarbons justifies consideration.

Virtually any mechanism for formation of products derived from dimerization of the alkyl halides (the C₁₂ hydrocarbons), including Schemes Ia and Ib, leads to the prediction that dimer formation is more favored when the concentration of alkyl halide is high and that of alkali naphthalene is low. When small portions of lithium naphthalene solution were injected into a stirred solution of 1,6-dibromohexane, initially $1.45 \times 10^{-1} M$, until the green color persisted, alkyl dimers were formed in 14% yield (8.4% dodecane, 2.4% 1-dodecene, 3.3% cyclododecane). Less than 5% dimers were formed in experiments in which lower concentrations of alkyl halide were injected into excess lithium naphthalene. The variation is in the predicted direction.

A more definitive test can be applied to the question of the mechanism of hexane formation. According to Scheme Ib, there are two likely principle sources for hexane, reactions 3 and 4. In either event, the process leading ultimately to hexane competes with

reaction 1. Reaction 1 will be first order and reaction 3 will be pseudo first order. Therefore, if reactions 1 and 3 were to determine the relative yields of hexane and C₆H₁₂, there would be no variations in these relative yields with variations in the concentration of alkali naphthalene. On the other hand, reaction 4 will be second order, with a rate dependence on the alkali naphthalene concentration. If reactions 1 and 4 were to determine the relative yields of hexane and C₆H₁₂, then the proportionate amount of hexane formed would decrease with decreasing alkali naphthalene concentration.

When small portions of lithium naphthalene solution were successively injected into a stirred solution of 1,6-dichlorohexane until the green color persisted, the hexane yield was 28% and the C₆H₁₂ yield was 16%, a yield ratio of hexane/C₆H₁₂ of 1.8. For experiments in which the alkyl halide was injected into excess lithium naphthalene (Table I), or in which it was slowly distilled into a stirred solution of lithium naphthalene, this yield ratio was 8. In similar experiments with 1,6-dibromohexane, the corresponding yield ratios were 0.35 and 0.93, respectively. Therefore, reaction 3 cannot account for more than a small portion of the hexane; it probably accounts for none. Reaction 4 is consistent with the data.

Reaction 4 leads to an alkali 1,6-hexylidene, the conceivable reactions of which include collapse to cyclohexane with ejection of an alkali atom, a process which might be called internal associative electron detachment. If this process were operative, some cyclohexane could arise through reaction 4. The ratio cyclohexane/1-hexene would be affected by the extent to which reaction 4 is important. However, in the reactions of 1,6-dibromohexane with lithium naphthalene

(9) For example, other processes might include the association and coupling of 6-halohehexylalkalies and reactions of 1,6-lithio- and 1,6-disodiohexanes with alkyl halides (see the last paragraph of this paper).

under the different conditions described in the paragraph just above, this ratio was the same within experimental error (2.2 for injection of alkyl halide into excess lithium naphthalene, 1.9 for successive injections of small amounts of lithium naphthalene into an alkyl halide solution), even though the hexane/C₆H₁₂ changed considerably. Therefore, it is indicated that the internal associative electron detachment is unimportant. Related evidence was adduced earlier in connection with reactions of 1,4-dihalobutanes and 1,5-dihalopentanes.⁴ Apparently the fate of the alkali 1,6-hexylide is reaction with alkali naphthalene.¹⁰

Counterion Control of Multiple Reduction. The reaction of 1,6-dichlorohexane with lithium naphthalene yields the four-electron reduction product (hexane) accompanied by only 1/8 as much two-electron reduction products (cyclohexane and 1-hexene). In contrast, the similar reaction of sodium naphthalene gives two-electron reduction products accompanied by only 1/8 as much hexane. This counterion variation effects a change in the product ratio hexane/C₆H₁₂ from 8 to 0.3. Thus, in this case counterion variation is an effective method for controlling the extent of reduction.

This effect can be understood in terms of Scheme Ib, incorporating reactions 1, 2, and 4 but omitting reaction 3, as discussed above. The hexane/C₆H₁₂ ratio is determined by the competitive reactions of a 6-chlorohexylalkali. Intramolecular reaction gives cyclohexane and 1-hexene, while further reaction with alkali naphthalene gives an alkali 1,6-hexylide leading to hexane. A metal ion effect on the relative rates of these reactions would account for the observations.

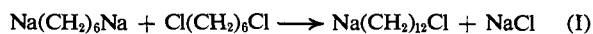
Such a metal ion effect is not only possible, it could have been anticipated on the basis of recent kinetic results. Reactions of alkali naphthalenes with primary alkyl fluorides in DME are sufficiently slow for rate

(10) It is conceivable that dodecane could arise by coupling of alkali 1,6-hexylides. However, independently formed simple alkyl radicals do not couple in the presence of alkali naphthalenes; they are scavenged by the alkali naphthalenes instead.^{3,4} By analogy, it seems unlikely that alkali 1,6-hexylides could couple rather than react with alkali naphthalene.

measurements by conventional means. Lithium naphthalene reacts 100 times as rapidly as sodium naphthalene.¹¹ Potassium naphthalene reacts more slowly yet and cesium naphthalene so slowly that no reaction was observed over the course of several days. With an alkyl chloride, it was observed qualitatively that cesium naphthalene reacts much more slowly than the other alkali naphthalenes, whose reactions are too fast to follow by conventional means. Thus, it is indicated that the reactivity order found for alkyl fluorides probably extends to alkyl chlorides as well.

This implies that the reaction of lithium naphthalene at the C-Cl end of 6-chlorohexyllithium can be expected to be much faster than the corresponding reaction of sodium naphthalene with 6-chlorohexylsodium. The competing intramolecular reactions might be expected to respond to metal ion variation in the opposite order. No data are available which are good analogies, but it is well known that simple alkyllithiums are less reactive than alkylsodiums in many kinds of reactions.¹²

Dimers from 1,6-Dichlorohexane. A minor puzzle is afforded by the fact that the reaction of 1,6-dichlorohexane with sodium naphthalene gives about 4% dodecane. From simple primary alkyl chlorides, only traces of alkyl dimers, if any, are found. This may be regarded as a rather trivial difference in behavior, but in any event, it is not obvious that Scheme I includes a method of accounting for it. Perhaps the dimer from 1,6-dichlorohexane arises from reactions of 1,6-disodiohexane in a sequence beginning with reaction I.



Disodiohexane has a built-in capacity for (internal) ion quadrupole formation, and this could affect its relative reactivity toward DME and 1,6-dichlorohexane.

Acknowledgment. We are grateful to the National Science Foundation for grants supporting this work.

(11) J. F. Garst and F. E. Barton, II, *J. Amer. Chem. Soc.*, **96**, 523 (1974).

(12) See, for example, G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, "Principles of Organometallic Chemistry," Methuen, London, 1968, p 32 ff.