with any degree of sophistication, our initial results indicate that formation of the cation **53** from axial and equatorial progenitors and coordination of **53** with nucleophiles from either direction is not a highly discriminatory process and that differences will probably be found to have steric roots.

Electron Transfer, Naphthalene Radical Anion, and Alkyl Halides

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In solvents like 1,2-dimethoxyethane (DME), naphthalene is readily reduced by alkali metals.[1] The resulting solutions of alkali naphthalenes are green, conducting, and paramagnetic. Consistent with these properties, alkali naphthalenes are formulated as ionic substances consisting of alkali cations and naphthalene radical anions.[2]

$C_{10}H_8$

$C_{10}H_8{}^-$
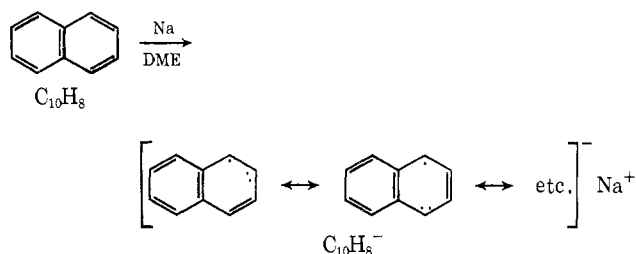
Sodium naphthalene is reactive toward oxygen, water, carbon dioxide, alkyl halides, aromatic hydrocarbons, and many other compounds. Its reactions with aromatic hydrocarbons are among the simplest.[2]
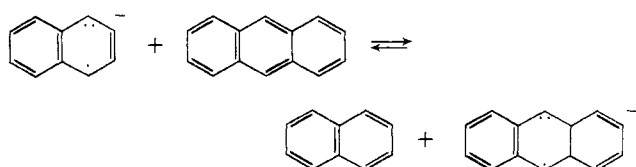

(metal counterions are omitted here and in many following equations)

Such reactions proceed to equilibrium positions which are determined largely by the relative electron affinities of the parent hydrocarbons. These are electron-transfer (ET) reactions, and many of the reactions of naphthalene radical anion fall into this class.

Alkali naphthalenes can also act as Lewis bases. Consider the reaction of sodium naphthalene with water:
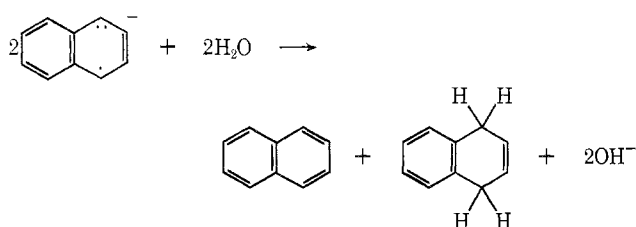
Bank and Closson, and more recently Bank and Bockrath,[3] have verified the reaction mechanism proposed earlier by Paul, Lipkin, and Weissman (eq 1).[4] In the

(1)

initial step of this process, naphthalene radical anion acts as a proton acceptor. In other reactions it acts in parallel fashion, *i.e.* as a base or a nucleophile.

Reactions of alkyl halides with naphthalene radical anion recently attracted our attention,[5] and that of
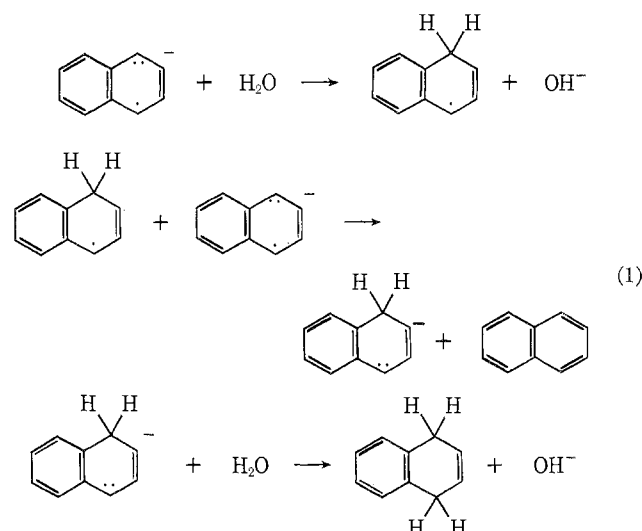
(1) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Amer. Chem. Soc.*, **58**, 2442 (1936).

(2) See the following for general background and references: (a) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," 3rd ed, Vol. I, Methuen, London, 1967, Chapter 1; (b) E. de Boer, *Advan. Organometal. Chem.*, **2**, 115 (1964); (c) B. J. McClelland, *Chem. Rev.*, **64**, 301 (1964); (d) M. Szwarc, "Carbanions, Living Polymers, and Electron-Transfer Processes," Interscience, New York, N. Y., 1968, Chapter VI.

(3) (a) S. Bank and W. D. Closson, *Tetrahedron Lett.*, 1349 (1965); (b) S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, **93**, 430 (1971).

(4) D. E. Paul, D. Lipkin, and S. I. Weissman, *ibid.*, **78**, 116 (1956).

(5) J. F. Garst, P. W. Ayers, and R. C. Lamb, *ibid.*, **88**, 4260 (1966).

other groups,[6,7] for several reasons. First, we were interested in the initial step. Both ET (electron transfer) and SN2 possibilities have been suggested.[8-10] Which is it? Or is it metal–halogen interchange? Or are there significant competitions among these possibilities? These questions are intrinsically interesting and further relate to the general question of ET–SN2 competitions in reactions of nucleophiles with alkyl halides.[11-14] Second, since earlier works reported the formation of alkyl dimers from similar reactions,[15] it seemed likely that there might be analogies with Wurtz reactions, the mechanisms of which are still uncertain. Third, it appeared that alkyl halide–sodium naphthalene reactions might be convenient sources of alkyl radicals. The reactivity of alkyl radicals toward naphthalene radical anion was unknown but potentially interesting.
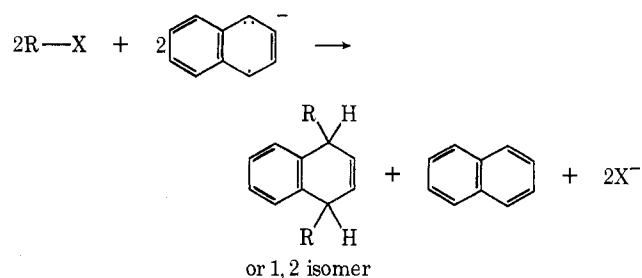
Several different kinds of products arise in reactions of alkyl halides with naphthalene radical anion. Alkylation results mostly in alkyl- and dialkyldihydronaphthalenes.[9,16] In addition, α- and β-alkylnaphtha-
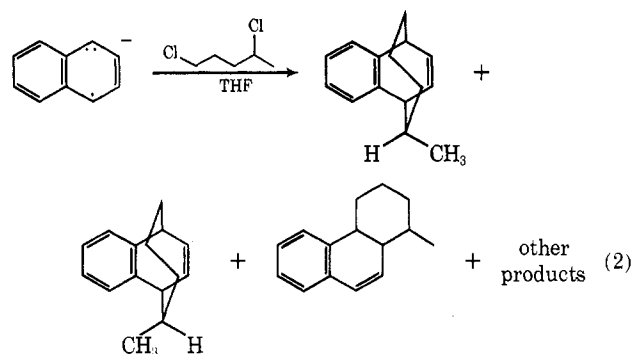
Monoalkylation

or 1,2 isomer
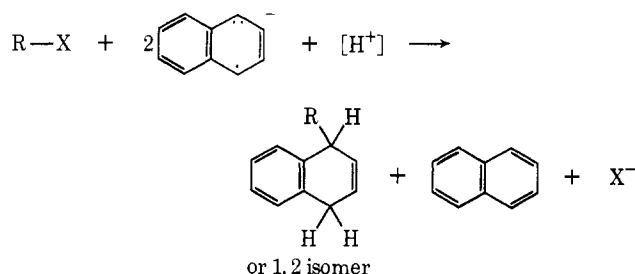
lenes may be formed.[9] Lipkin has studied the alkyla-
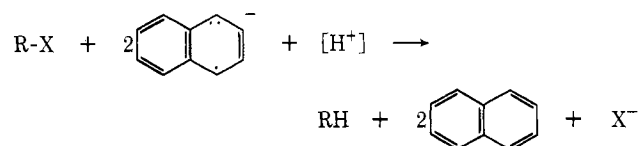
Dialkylation

or 1,2 isomer

tion products in detail and has reported some synthetically useful reactions (eq 2).[9]

(2)

The alkyl halides also suffer reduction. In these processes, the naphthalene is completely regenerated.

Reduction

The reactant proton is derived from the solvent. If the solvent is DME, there is concomitant production of methyl vinyl ether and methoxide ion. Bimolecular

Bimolecular Reduction

or RH + olefin
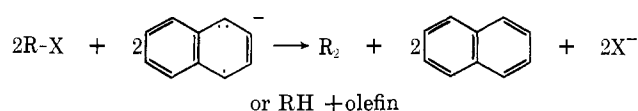
reduction is an analog of the Wurtz reaction.

The distribution of reaction products depends strongly on the nature of the halogen involved and somewhat on the nature of the alkyl group and the reaction conditions. Some details will be discussed later, but is noted here that bimolecular reduction products can account for as much as 70% of the alkyl halide consumed in reactions of alkyl iodides, and that for alkyl bromides, chlorides, and fluorides typical corresponding figures are 10, 1, and 0%, respectively.

Considering both our own results and those of other investigators, we have been led to Scheme I as the
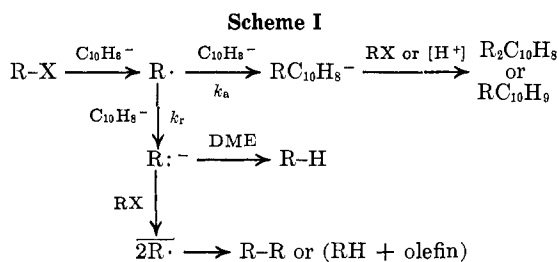
Scheme I

general mechanism of these reactions. (*Note: In this scheme, and elsewhere in this Account, metal counterions, regenerated aromatic hydrocarbons, and solvent-derived products are omitted to avoid cluttering. The reader must not construe that this implies that radical anions and carbanions are not associated with metal counterions.*)

(6) G. D. Sargent, J. N. Cron, and S. Bank, *J. Amer. Chem. Soc.*, **88**, 5363 (1966).

(7) S. J. Cristol and R. V. Barbour, *ibid.*, **88**, 4262 (1966); **90**, 2832 (1968). These works involve biphenyl radical anion, the reactions of which appear to be analogous with those of naphthalene radical anion.

(8) D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **51**, 1375 (1955); E. Warhurst and R. Whittaker, *ibid.*, **63**, 707 (1966), and intervening papers.

(9) D. Lipkin, G. J. Divis, and R. W. Jordan, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **13**, D60 (1968).

(10) G. J. Hoijtink, *Chem.-Ing.-Tech.*, **35**, 333 (1963).

(11) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956); *Bull. Soc. Chem. Fr.*, 1418 (1963).

(12) N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Amer. Chem. Soc.*, **88**, 5662 (1966), and later papers.

(13) G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966).

(14) K. A. Bilevich, N. N. Bubov, and O. Yu. Okhlobystin, *Tetrahedron Lett.*, 3465 (1968).

(15) W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Chem. Ber.*, **47**, 473 (1914).

(16) N. D. Scott and J. F. Walker, U. S. Patent 2,150,039 (March 7, 1939); *Chem. Abstr.*, **33**, 4602[6] (1939).

Ionic aggregation at least to ion pairs, and possibly to higher aggregates, is to be assumed.[2d]) The heart of Scheme I is the initial step, an electron-transfer reaction producing an alkyl radical, and the immediately following competitive reactions, which invoke sodium naphthalene as a scavenger for the initially formed alkyl radicals. Alkyl radicals either combine with sodium naphthalene or are reduced by it. This is a novel competition, but it has analogy in the well-known combination–disproportionation reactions of simple alkyl radicals. The ET is analogous to the conventional disproportionation.

The remainder of Scheme I deals with subsequent steps in the pathways to alkylation, reduction, and bimolecular reduction products. The bimolecular reduction pathway presents interesting problems and cannot be considered as well supported at this time as the other pathways.

The rest of this Account details some of the evidence supporting Scheme I. In addition, some related chemistry is explored. It is convenient to consider the mechanisms of formation of the various types of products in turn, beginning with the reduction products.

**Mechanism of Formation of Reduction Products.** There are a number of conceivable pathways to reduction products. For example, the initial step could be metal–halogen interchange, producing an alkyl anion (*i.e.*, an alkylsodium) directly (eq 3). Initial ET,

$$R\text{-}X \ + \ \text{[naphthalene radical anion]} \ \longrightarrow$$

$$\tag{3}$$
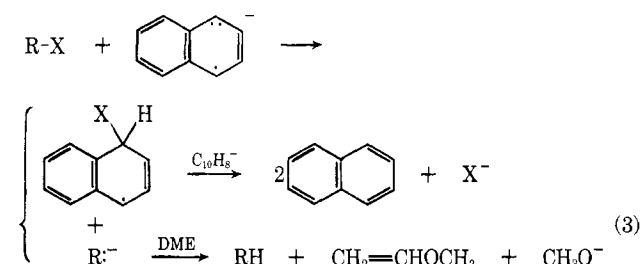
however, would lead to intermediate alkyl radicals (eq 4). These alkyl radicals might react with solvent

$$R\text{-}X \ + \ \text{[naphthalene radical anion]} \ \longrightarrow \ R\cdot \ + \ X^- \ + \ \text{[naphthalene]} \tag{4}$$
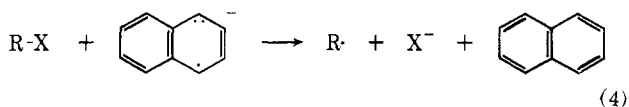
(eq 5) or they might suffer some other fate, such as

$$R\cdot \ + \ CH_3OCH_2CH_2OCH_3 \ \longrightarrow$$

$$\tag{5}$$
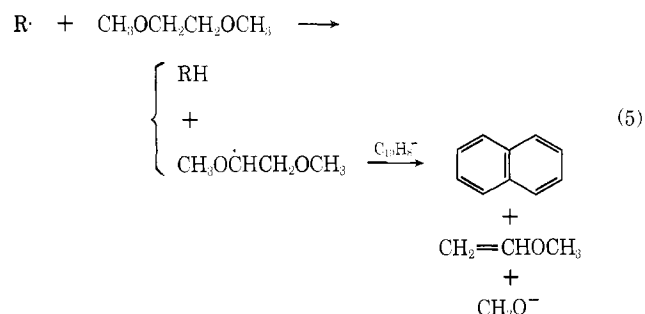
reaction with naphthalene radical anion, as indicated in Scheme I.

To test for alkyl radical intermediates, we employed 5-hexenyl halides.[5] Since 5-hexenyl radicals undergo

Table I

Reduction and Bimolecular Reduction Products of Reactions of 5-Hexenyl Halides with Sodium Naphthalene in DME[a]

5-Hexenyl halide	1-Hexene, %	Methyl-cyclopentane, %	$C_{12}H_{22}$, %	1,5-Hexadiene, %
F	54	4	0	0
Cl	50	7	<3	Tr
Br	40	10	5	Tr
I	11	2	43	3

[a] Data are from ref 18, 19, and 22. Yields correspond to alkyl halide consumed. Because solution homogeneity during reaction could not be guaranteed or controlled for reactions of alkyls chloride, bromides, and iodides, the variations in the ratios (1-hexene/methylcyclopentane) are probably not significant. The similarities among the product distributions are more striking than the differences, except for the marked increase in alkyl dimer found in going to an alkyl iodide from another alkyl halide.

a facile cyclization to cyclopentylmethyl radicals,[17,18] the products of reactions of 5-hexenyl halides with sodium naphthalene might contain cyclopentylmethyl groups if alkyl radicals were intermediates. The reduction products bear out this expectation (Table I).

The finding of cyclic reduction products does not rule out the possibility that alkyl anions, but not radicals, are intermediates, since 5-hexenyl anions could be cyclizing. However, control experiments suggest that the maximum extent to which 5-hexenylsodium might cyclize in DME is about 3%.[5,18] Since the observed extents of cyclization are greater than this, there must be intermediates other than 5-hexenylsodium. 5-Hexenyl radicals are the most viable candidates.

If the fate of the 5-hexenyl radical intermediates were to cyclize and react with solvent competitively, then only methylcyclopentane would be produced, not 1-hexene, since cyclizations of 5-hexenyl radicals are much faster than their reactions with solvents like toluene and DME[17,18] (eq 6). In fact, more 1-hexene is produced


$$\tag{6}$$
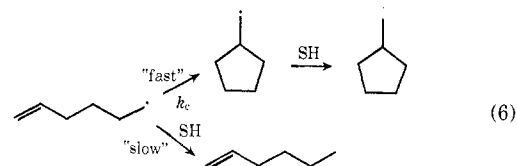
than methylcyclopentane. Thus, 5-hexenyl radicals, if they are intermediates, must suffer some fate other than cyclization and reaction with solvent.

A reasonable hypothesis is that the cyclization of the intermediate 5-hexenyl radicals competes with their reactions with sodium naphthalene (eq 7). This implies that *both* alkyl radicals and alkyl anions are intermediates along the path to reduction products.
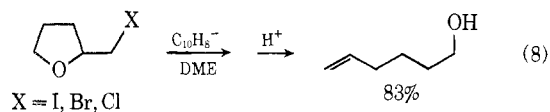
Other facts offer direct support for the intermediacy of alkyl anions. Tetrahydrofurfuryl halides react with sodium naphthalene to give only 4-penten-1-ol as the

(17) R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Amer. Chem. Soc.*, **85**, 3482 (1963).
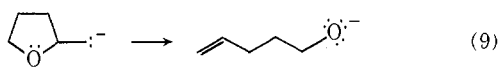
(18) J. F. Garst, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **13**, D65 (1968).
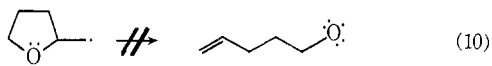
(7)
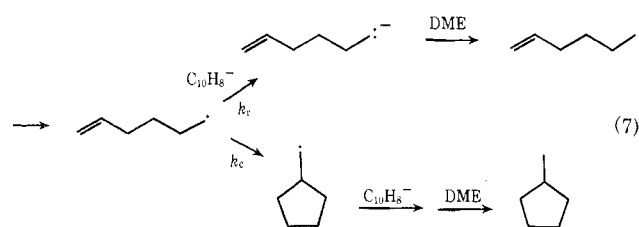
reduction product[18,19] (eq 8). This is the anticipated

(8)

result if tetrahydrofurfuryl anions are intermediates, since they are known to open[20] (eq 9). On the other


(9)

hand, tetrahydrofurfuryl radicals do not open[18] (eq 10).

(10)

Thus, if tetrahydrofurfuryl radical intermediates were not reduced to anions, the observed 4-penten-1-ol would not have been expected.

It should also be noted that no methyltetrahydrofuran could be detected from reactions of tetrahydrofurfuryl halides with sodium maphthalene. Methyltetrahydrofuran would be an expected product if intermediate tetrahydrofurfuryl radicals reacted with solvent. Its absence is consistent with the proposition that intermediate radicals are scavenged by sodium naphthalene (eq 11).

(11)
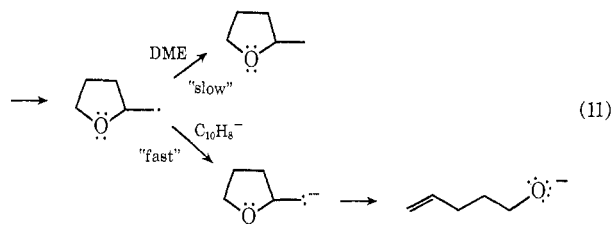
Another experimental fact supporting alkyl anion intermediates is the finding of Bank and Bank that addition of MgBr₂ to reacting solutions of alkyl halides and sodium naphthalene in THF diverts reduction products to Grignard reagents.[21] This result can be interpreted as trapping of intermediate alkylsodiums by MgBr₂ (eq 12).

$$R:^- Na^+ \xrightarrow{MgBr_2} RMgBr + NaBr \qquad (12)$$
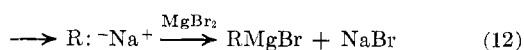
A third piece of direct evidence for alkyl anion intermediates relates specifically to reactions of lithium naphthalene. When D₂O was added to the product mixture following a reaction of lithium naphthalene with 5-hexenyl chloride, the 1-hexene and methylcyclo-

pentane formed were both about 35% monodeuterated.[19] This implies the presence of 5-hexenyllithium and cyclopentylmethyllithium in the product mixture.

Returning now to the question of alkyl radical intermediates, it is clear that if cyclization of 5-hexenyl radicals is being limited by competition with their reactions with sodium naphthalene, then an increase in the concentration of sodium naphthalene should lead to an increase in the ratio 1-hexene/methylcyclopentane. With 5-hexenyl iodide, bromide, and chloride, this prediction is not easily tested quantitatively because the reactions are so fast that they appear to be complete within the time of ordinary mechanical mixing. Qualitative confirmation of the prediction was obtained from experiments with 5-hexenyl chloride.[19]

Quantitative data were sought from reactions of 5-hexenyl fluoride.[22] It was hoped that sodium naphthalene–alkyl fluoride reactions would be slow, but that they would follow the same pathways as the other alkyl halides.

The reactions of sodium napthalene with 5-hexenyl, hexyl, and octyl fluorides *are* slow, the second-order rate constants being about $5 \times 10^{-4} M^{-1} sec^{-1}$.[22] The products are similar to those obtained from reactions of other alkyl halides.

As the initial concentration of sodium naphthalene varies from ~$3 \times 10^{-4} M$ to ~$5 \times 10^{-3} M$, the ratio 1-hexene/methylcyclopentane varies from ~2 to ~20, adhering to the form of an integrated expression based on Scheme I. From these data, k_r/k_o is evaluated as about $1 \times 10^4 M^{-1}$. An independent determination of k_c for a reaction in a different medium gave ~1×10^5 sec^{-1}.[23] Assuming no medium effect on k_c, this places k_r at ~$1 \times 10^9 M^{-1} sec^{-1}$, near the diffusion-controlled limit of about $10^{10} M^{-1} sec^{-1}$.

Thus, there is substantial evidence that both alkyl radicals and alkyl anions are intermediates along the pathway to reduction products, as indicated in Scheme I.

Mechanism of Formation of Alkylation Products. Since both mono- and dialkylation products are formed in reactions of sodium naphthalene with alkyl halides, mechanisms must be considered for two alkylation steps. The first will be considered below, then the second.

The discussion above, supporting the reduction pathway of Scheme I, does not exclude formation of alkylation products through other pathways. However, since the conclusion has been reached that at least *part* of the initial reaction between sodium naphthalene and an alkyl halide is ET, a major question is, "Could there be an initial S$_N$2 reaction competing with the initial ET step?" If so, then alkylation products could arise through initial S$_N$2 reactions while reduction products arise from initial ET steps (eq 13).

The lack of effect of halogen variation on the distribution of reduction and monoalkylation products

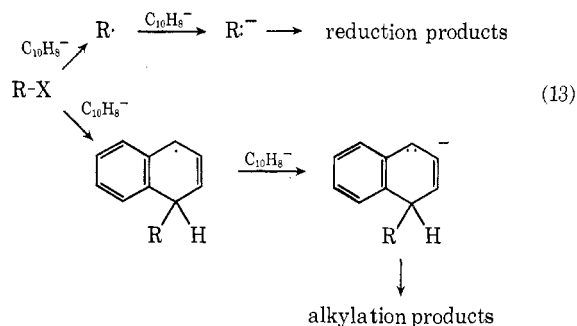(19) J. T. Barbas and J. F. Garst, unpublished observations.
(20) L. A. Brooks and H. R. Snyder in "Organic Syntheses," Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1955, p 698.
(21) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969).
(22) J. F. Garst and F. E. Barton, II, *ibid.*, 587 (1969).
(23) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).
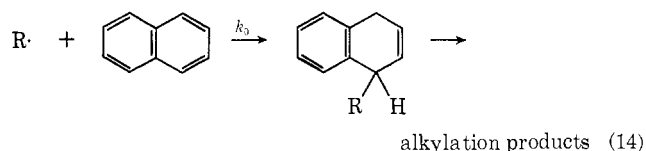
$$(13)$$

alkylation products

Table II

**Reduction–Alkylation Product Distribution in Reactions of Sodium Naphthalene with Primary Alkyl Halides in DME[a]**

Alkyl halide	Reduction, %	Alkylation, %	Bimolecular reduction, %
5-Hexenyl iodide	41	(52)	7
5-Hexenyl bromide	47	(48)	5
5-Hexenyl chloride	55	(45)	0
5-Hexenyl fluoride	58	(42)	0
1,4-Diiodobutane	55	44	0
1,4-Dibromobutane	56	(44)	0
1,4-Dichlorobutane	59	(41)	0
1,5-Diiodopentane	57	50	0
1,5-Dibromopentane	57	(43)	0
1,5-Dichloropentane	63	(37)	0

[a] Data are from ref 19 and 24–26. Conditions and nature of reactions suppressed dialkylation and bimolecular reduction. Figures not in parentheses are results of direct analyses; in parentheses, by difference; "100%" mass balances are reported here for reactions of 1,4-diiodobutane and 1,5-diiodopentane. Sargent and Lux also found that reduction, bimolecular reduction, and alkylation products account quantitatively for the reactants.[27] The average yield of reduction products is 58%, corresponding to $k_r/k_a = 1.4$. Entries for 5-hexenyl iodide and bromide are not included in this average, but they are regarded as consistent with it, considering the uncertainty resulting from the incomplete suppression of bimolecular reduction and, possibly, dialkylation products in those cases.

mitigates against this possibility. ET and S$_N$2 reactions must have somewhat different transition states. Therefore, variation of halogen should affect their rates differently. The distribution between reduction and alkylation products has been examined for alkyl fluorides, chlorides, bromides, and iodides under conditions in which bimolecular reduction and dialkylation products are either suppressed or absent.[19,24–26] These data are given in Table II.

Considering the extreme range of halogens used, it is not reasonable to imagine that the effects of halogen variation run exactly parallel for the ET and S$_N$2 reactions. Since the ET pathway is established for reduction products, alkylation products must also arise through intermediate alkyl radials. Scheme I accommodates this by involing competitive ET and radical combination reactions of sodium naphthalene and intermediate alkyl radicals. The data place a value of ~1.4 on k_r/k_a for primary alkyl radicals reacting with sodium naphthalene at room temperature.

Independent evidence on the alkylation mechanism comes from studies of alkyl group variation. Sargent and Lux found more alkylation in reactions of *tert*-pentyl iodide with sodium naphthalene in DME than in reactions of *n*-pentyl iodide, with *sec*-pentyl iodide being intermediate.[27] Considering the reluctance of *tert*-alkyl halides to undergo S$_N$2 reactions, this also seems inconsistent with alkylation through an initial S$_N$2 step. Taken together, the direction of the effect of alkyl group variation and the lack of effect of halogen variation leave little doubt that there are no significant initial S$_N$2 steps in any reaction of sodium naphthalene with simple alkyl halides in DME.

An alternative alkylation route involves addition of alkyl radicals to naphthalene itself, rather than combination of alkyl radicals with naphthalene radical anion (eq 14).[10] There are two grounds for ruling this out:

alkylation products   (14)

(1) the rate constant, k_0, is probably too small to permit

this reaction to compete with reactions of the alkyl radicals with naphthalene radical anion;[28] (2) variation in the amount of naphthalene in the reaction mixtures does not affect the product distribution.[27]

Incidentally, several of the experimental results cited in this section mitigate against the possibility that naphthalene dianion (C$_{10}$H$_8{}^{2-}$) is an intermediate involved in a product-determining step. Further, the fact that the disappearance of C$_{10}$H$_8{}^-$ is first-order in C$_{10}$H$_8{}^-$ (and first-order in RF),[22] in reactions of sodium naphthalene with alkyl fluorides, rules out the involvement of C$_{10}$H$_8{}^{2-}$ as a reactant or a product in steps which determine $-d[C_{10}H_8{}^-]/dt$.

The second alkylation is presumed to proceed from an anion derived from an alkyldihydronaphthalene (RC$_{10}$H$_8{}^-$). Sargent and Lux noted the absence of


RC$_{10}$H$_8{}^-$
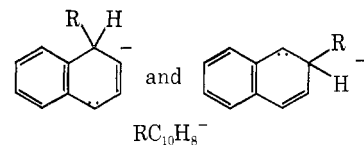
dialkylation products from reactions of *tert*-pentyl and neopentyl iodides with sodium naphthalene.[27] This suggests that the second alkylation steps are simple S$_N$2 reactions. Related observations in our laboratories are

(24) J. F. Garst, J. T. Barbas, and F. E. Barton, II, *J. Amer. Chem. Soc.*, **90**, 7159 (1968).

(25) J. F. Garst and J. R. Barbas, *ibid.*, **91**, 3385 (1969).

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

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

(28) The corresponding rate constant for reactions of phenyl radicals with benzene has been estimated as 2×10^3 M^{-1} sec^{-1} (D. F. DeTar, *J. Amer. Chem. Soc.*, **89**, 4058 (1967)). Naphthalene is about 20 times as reactive toward phenyl radicals as benzene (D. R. Augood and D. H. Williams, *Chem. Rev.*, **57**, 123 (1957); see Table 8B, p 158). Assuming that phenyl radicals and primary alkyl radicals are of comparable reactivity toward aromatics, one estimates k_0 as 4×10^4 M^{-1} sec^{-1}, suggesting that the ratio of naphthalene to naphthalene radical anion present in solution would have to be about 10^5 in order for alkyl radicals to react at comparable rates with the two substrates.

that reactions of various tertiary and neopentyl halides give rise to red product solutions, even when excess halide is present.[19] This is not true of similar reactions of primary and secondary halides. The intermediate anions $RC_{10}H_8{}^-$ are expected to be red,[29] and their persistence could be attributed to the unreactivity of tertiary and neopentyl halides in SN2 reactions. More detailed studies on this point are required.

Mechanism of Formation of Bimolecular Reduction Products. Sargent and coworkers provided evidence that bimolecular reduction products are *not* formed in conventional SN2 reactions of intermediate alkyl anions (alkylsodiums) with alkyl halides. Their original data on dimer distributions from equimolar mixtures of n-propyl and isopropyl iodides were reinforced by a later finding that neopentyl iodide gives a high (∼70%) yield of bineopentyl, which could hardly arise in a conventional SN2 reaction of neopentyl-sodium with neopentyl iodide. On such grounds, they proposed the following bimolecular reduction pathway, involving combination and disproportionation of initially formed radicals.[6,27]

$$R\text{-}X \xrightarrow{C_{10}H_8{}^-} R\cdot \xrightarrow{R\cdot} R\text{-}R \text{ (or } RH + \text{olefin)}$$
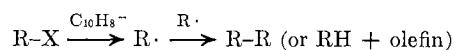
However, reactions of 1,4-diiodobutane and 1,5-diiodopentane with sodium naphthalene in DME give no sign of bimolecular reduction products. In fact, an essentially quantitative product balance is obtained in which the only products are those containing but *one* residue of the starting alkyl halide per molecule.[19,25,26] For example, from the reaction of 1,4-diiodobutane with sodium naphthalene, cyclobutane, ethylene, and monoalkylation products ($C_{14}H_{16}$) account for 99% of the starting alkyl halide. Further, the fact that the reduction product yields (Table II) from these reactions are the same as from reactions of simple primary alkyl halides suggests that the reduction and alkylation pathways of Scheme I apply, with the slight variation that the carbanions formed decompose directly to reduction products, rather than reacting with solvent.
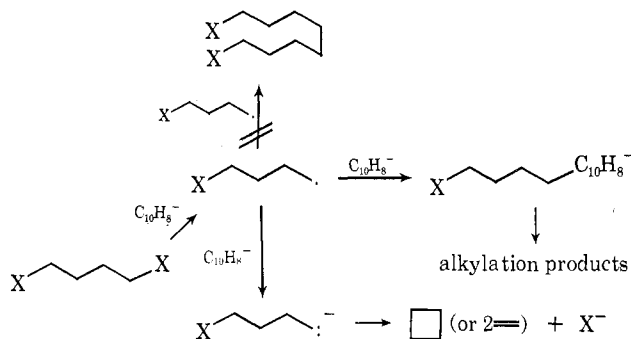
Since the intermediate ω-haloalkyl radicals do not react among themselves, and since in other reactions (e.g., those with sodium naphthalene) they behave just as do simple primary alkyl radicals, it is very difficult to

understand why their behavior in radical dimerization reactions should be different from that of simple alkyl radicals. More likely, all initially formed alkyl radicals suffer reduction by, or combination with, sodium naphthalene.[26]

Bank and Bank support this conclusion with independent data.[21] They found that the presence of $MgBr_2$ interferes with the formation of alkyl dimers in reactions of alkyl iodides with sodium naphthalene in THF. If the dimers arise from combination of initially formed radicals, this should not have been the result, but if the dimers arise through alkylsodium intermediates, then the observations are rationalized by the assumption that $MgBr_2$ intercepts these, converting them to less reactive Grignard reagents. Bank and Bank pointed out that their data do not rule out the possibility that *part* of the alkyl dimers arise through coupling of initially formed radicals, but on the basis of other evidence, it seems more likely that such coupling is insignificant.

Part of the other evidence has already been cited: the lack of dimerization in reactions of 1,4-diiodobutane and 1,5-diiodopentane. Additional evidence of the same type, but from a different system, is the absence of alkyl dimers and disproportionation products from reactions of tetrahydrofurfuryl iodide with sodium naphthalene.
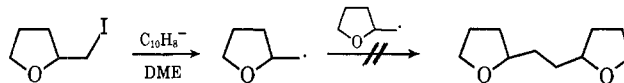
As mentioned earlier, this reaction leads to the same yield of 4-penten-1-ol as do reactions of tetrahydrofurfuryl bromide and chloride.[19]

Thus, it appears that bimolecular reduction products are formed through alkylsodium intermediates, but not in SN2 reactions of these with alkyl iodides, posing a dilemma to which the bimolecular reduction pathway of Scheme I is a resolution. It is patterned after mechanisms of reactions of alkyllithiums with alkyl halides, for which there is abundant evidence indicating free-radical intermediates. The first step of these reactions can be represented as in eq 15. The geminate

$$(R\mathord:{}^-,Li^+)_n + R'X \longrightarrow \overline{R\cdot,R'\cdot,Li^+,X^-,(R\mathord:{}^-,Li^+)_{n-1}} \quad (15)$$
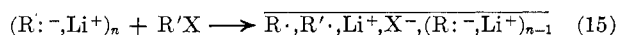
radical pairs may then combine, disproportionate, or diffuse apart. The intermediate radicals have been trapped,[11] observed by esr,[30,31] inferred from chemically induced nuclear spin polarization,[32,33] and inferred from stereochemical experiments.[34]

Although the bimolecular reduction pathway of Scheme I accommodates the experimental facts discussed above, there are other results which are of doubtful consistency with it (see the following two sections). It is at this time the most viable mechanism,

(29) (a) D. H. Richards and M. Szwarc, *Trans. Faraday Soc.*, **55**, 1644 (1959); (b) see ref 3b; (c) M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *J. Amer. Chem. Soc.*, **91**, 6505 (1969). These references document the spectra and color of anions of the type $RC_{10}H_8{}^-$, where R may be hydrogen or some other group.

(30) G. A. Russell and D. W. Lamson, *ibid.*, **91**, 3967 (1969).
(31) H. Fischer, *J. Phys. Chem.*, **73**, 3834 (1969).
(32) H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Amer. Chem. Soc.*, **91**, 746 (1969), and earlier works.
(33) A. R. Lepley and R. L. Landau, *ibid.*, **91**, 748 (1969), and earlier works.
(34) J. Sauer and W. Braig, *Tetrahedron Lett.*, 4275 (1969).

Table III
Reduction Products from Reactions of 1,4- and
1,5-Dihaloalkanes with Sodium Naphthalene in DME[a]

Dihaloalkane	Cyclo-alkane, %	Ethylene, %	n-Alkane, %
1,4-Diiodobutane	51	~4	0
1,4-Dibromobutane	56	~2	0
1,4-Dichlorobutane	59	Tr	0

Dihaloalkane	Cyclo-alkane, %	1-Pentene, %	n-Alkane, %
1,5-Diiodopentane	42	15	Tr
1,5-Dibromopentane	53	2	1.6
1,5-Dichloropentane	63	Tr	1.8

[a] Data are from ref 19, 25, and 26. The italicized figure was obtained by difference, the others by direct measurement.
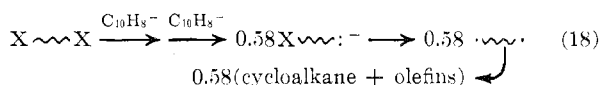
but other alternatives may have to be considered later. Among such alternatives are associative electron detachment[12,13,35] and unconventional nucleophilic displace-

$$R\cdot + R:^- \longrightarrow R-R + e^- \qquad (16)$$
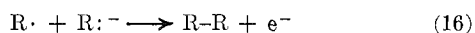
ment (eq 17), perhaps one in which the association of the metal ion with the developing halide ion plays a dominant role.

$$R:^-,Na^+ \xrightarrow{RI} \begin{bmatrix} R^{\delta^-}\cdots R \\ Na^+ \quad I^{\delta^-} \end{bmatrix} \longrightarrow \begin{array}{c} R-R \\ + \\ NaI \end{array} \qquad (17)$$
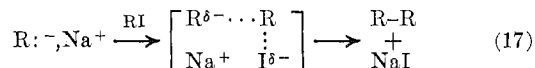
Biradicals from α,ω-Dihaloalkanes? Application of Scheme I to dihaloalkanes leads to the following kind of sequence (eq 18). It appears that this mechanism

$$X\sim\sim X \xrightarrow{C_{10}H_8^-} \xrightarrow{C_{10}H_8^-} 0.58X\sim\sim:^- \longrightarrow 0.58 \cdot\sim\sim\cdot \qquad (18)$$
$$0.58(\text{cycloalkane} + \text{olefins})$$

predicts the same distribution of cycloalkane and olefins from any particular biradical intermediate, independent of the halogen present in the precursor of that intermediate. Table III gives some relevant data.

It is seen that the prediction is incorrect; there are halogen effects on the cycloalkane–olefin distribution. In the cases which might proceed through 1,5-pentadiyl, the effects are rather pronounced. The ratio k_s/k_e would vary as follows if the biradical interpretation were applied to the data: I, 2.8; Br, 26; Cl, >100.
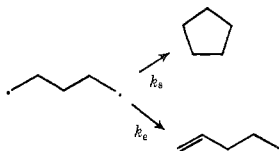
Although it may be possible to "save" the biradical mechanism by invoking biradical conformational effects, mechanism changes with halogen variation, or other factors, these data place it under suspicion. By extension to corresponding intermolecular reactions, the bimolecular reduction pathway of Scheme I is made suspect.

Chemically Induced Dipole Nuclear Polarization. Reactions proceeding through free-radical intermediates may generate diamagnetic products which are initially formed with nonequilibrium nuclear spin state populations.[36] These give rise to product nmr spectra in which certain lines are up to hundreds or thousands of times more intense than normal. Alternatively, the lines may appear as negative peaks spanning a similar intensity range.

Reactions of alkyl halides with sodium naphthalene give rise to nuclear spin polarized reduction and bimolecular reduction products provided they are carried out in magnetic fields of a few to a few hundred gauss.[37,38] This supports mechanisms, like Scheme I, in which free alkyl radicals are intermediates. The nature of the observed polarizations is at least qualitatively understood in terms of Scheme I and the radical pair theory of CIDNP.[39,40]

The lack of polarization of bimolecular reduction products in cases of reactions run in large magnetic fields is puzzling. For example, the 2,3-dimethylbutane produced in the reaction of isopropyl iodide with sodium naphthalene in 5000 G shows a normal nmr spectrum.[41] The bimolecular reduction pathway of Scheme I, considered together with the radical pair theory,[39,40] seems to predict that these products should be polarized. This point is under investigation.

(35) E. E. Ferguson, *Accounts Chem. Res.*, **2**, 110 (1969).

(36) H. Fischer and J. Bargon, *ibid.*, **2**, 110 (1969). Leading references to the earlier work of these authors and of H. R. Ward and R. G. Lawler are given.

(37) J. F. Garst, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **11**, 8 (1970).

(38) J. F. Garst, R. H. Cox, J. T. Barbas, R. D. Roberts, J. I. Morris, and R. C. Morrison, *J. Amer. Chem. Soc.*, **92**, 5761 (1970).

(39) G. L. Closs, *ibid.*, **91**, 4552 (1969); G. L. Closs, C. E. Doubleday, and D. R. Paulson, *ibid.*, **92**, 2185 (1970); G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554; **92**, 2183, 2186 (1970).

(40) R. Kaptein and J. L. Oosterhoff, *Chem. Phys. Lett.*, **4**, 195, 214 (1969).

(41) J. F. Garst, J. T. Barbas, J. I. Morris, and R. H. Cox, unpublished results.