to another if the initial alkylation proceeded through an SN2 displacement. However, yield data obtained using the usual procedure of direct mixing of reactants by injection would be unsuitable for this purpose. The tendency of alkyl halides to yield dimeric hydrocarbon products (R_2) varies widely from one halogen to another. It is probable that the rates of the second step of alkylation similarly vary with halogen. It is therefore necessary to correct the yield data for the occurrence of these superfluous alkyl halide consuming reactions, or to carry out the reactions in such a fashion that they are suppressed. We have taken the latter course.

Reactions of 5-hexenyl iodide, bromide, and chloride were carried out by slowly evaporating the 5-hexenyl halides into stirred, concentrated (*ca.* 0.1 *M*) solutions of sodium naphthalenide maintained at 25°.[8] The data are summarized in Table I.

Table I. Yield Data for Reactions of Sodium Naphthalenide with 5-Hexenyl Halides in Evaporation Experiments[a]

Halide	R_2,[b] %	RH,[c] %	(RH + R_2), %
Iodide	11	40	51
	7	41	48
Bromide	5	47	52
	7	41	48
Chloride	0	55	55
	0	52	52
	0	54	54
Fluoride	0	58	58

[a] Yields are based on alkyl halide consumed. Analyses were by vpc on polyphenyl ether (20 ft × 0.25 in.) and fluorosilicone QF-1 (10 ft × 0.25 in.) columns. [b] Only 1,11-dodecadiene was detected as a dimer formed in these experiments, although 6-heptenylcyclopentane is also formed in direct injection experiments. The small yields of dimer reported in this column probably reflect the fact that some droplets of alkyl halides condensed above the surface of the sodium naphthalenide and ran down into the solutions. The high local concentrations of RX led to small amounts of dimers. [c] RH consists mainly of 1-hexene, although small amounts of methylcyclopentane are also formed. The total is reported in this column. The ratio (1-hexene/methylcyclopentane) was 13–20 for most of these experiments.

Dimer (R_2) was suppressed, but not completely eliminated, presumably due to experimental imperfections (see footnote to Table I). Even so, the variations in yield of reduction product (RH) are minor, the yield in each case being 50 ± 10%. Further, when the small amounts of dimer formed are taken into account in any of several possible ways, the variations are decreased. The total yield (RH + R_2), for example, is 53 ± 5%. This is true in spite of the extreme variation in the nature of the halogen (iodine through fluorine). Clearly halogen atoms are not bound in any intimate way into any of the species whose direct reactions account for the partitioning of products.[9] The partitioning must therefore take place at some stage of the mechanism after the halogen atoms have departed from the alkyl halide reactant molecules. This is inconsistent with alkylation through an initial SN2 displacement, but it is quite consistent with mechanisms in which an initially formed radical is partitioned along two pathways of reaction.[10]

One possible alkylation pathway is represented by eq 1 followed by eq 4.[7] We prefer eq 1 followed by eq 7, although the data reported herein do not permit

$$:\mathrm{Naph}\cdot^{-} + \mathrm{R}\cdot \longrightarrow :\mathrm{Naph{-}R}^{-} \qquad (7)$$

the rigorous exclusion of the former alternative. However, since reaction 2 is probably diffusion controlled,[1,3] it seems unlikely that reaction 4 could compete with it, except in the presence of a large excess of naphthalene. Reaction 7, on the other hand, involves the same reactants as reaction 2.

The results reported in the concomitant communication of Sargent and Lux complement ours.[11] Considering all these data *in toto*, it is apparent that no significant amount of initial SN2 alkylation of naphthalenide occurs in any of the systems examined. Alkylation proceeds, instead, through radical intermediates in every case.

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John F. Garst, John T. Barbas, Franklin E. Barton, II
Department of Chemistry, The University of Georgia
Athens, Georgia 30601

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[8] This procedure was first suggested to the authors by T. D. Walsh. If perfectly executed, both *dimeric* hydrocarbons (R_2) and dialkylated naphthalenide (R–Naph–R) would be completely absent from the products. In effect, the procedure guarantees that the fate of all alkyl halide molecules is to react with sodium naphthalenide, and not with other anions generated by the reaction. This is the desired situation for the present yield comparisons. In addition, the procedure ensures a uniform temperature. In direct mixing experiments this is a problem because the reactions are so fast and exothermic that adiabatic heating occurs during mixing and reaction.

[9] This conclusion is independent of the nature of the products formed competitively with RH and R_2. The assumption that these are alkylation products of the types previously reported is supported by their vpc characteristics, as well as by the infrared and nmr spectra of materials isolated from some experiments. They were not examined in further detail.

(10) Although only primary halides were examined in this work, this conclusion extends to secondary and tertiary halides if the reasonable assumption is made that initial SN2 reactions are less likely for these substrates than for primary ones.

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

Reactions of Aromatic Radical Anions. III. Evidence for an Alkyl Radical–Radical Anion Combination Mechanism for Alkylation of Sodium Naphthalenide with Alkyl Halides[1]

Sir:

The reaction of sodium naphthalenide (**1**) with alkyl halides in 1,2-dimethoxyethane yields a mixture of aliphatic hydrocarbons (**2–4**),[2] alkylated dihydronaphthalenes (**5–8**),[3–5] and alkylnaphthalene (**9**).[4,5]

The formation of aliphatic products (**2–4**) involves the intermediacy of alkyl free radicals (R·) generated by

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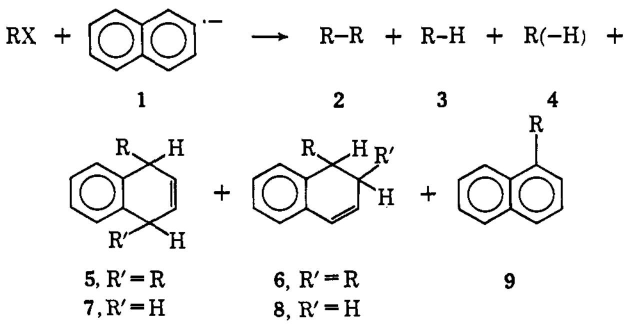
(1) Part II: G. D. Sargent and M. W. Browne, *J. Am. Chem. Soc.*, **89**, 2788 (1967).

(2) G. D. Sargent, J. N. Cron, and S. Bank, *ibid.*, **88**, 5363 (1966).

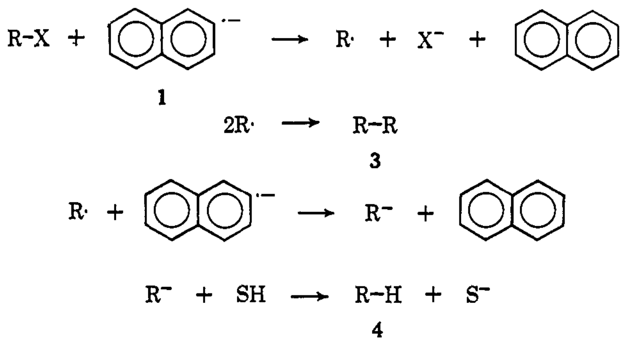
(3) The formation of dialkyldihydronaphthalenes in this reaction was first reported by N. D. Scott and J. F. Walker, U. S. Patent 2,150,039 (March 7, 1939).

(4) The reaction of **1** with 1,4-dichloroalkanes has been investigated. Products analogous to **5**, **6**, and **9** are reported: (a) D. Lipkin, G. J. Divis, and R. W. Jordan, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; *Preprints, Div. Petrol. Chem.*, **13**, D61 (1968); (b) D. Lipkin, F. R. Galiano, and R. W. Jordan, *Chem. Ind.* (London), 1657 (1963).

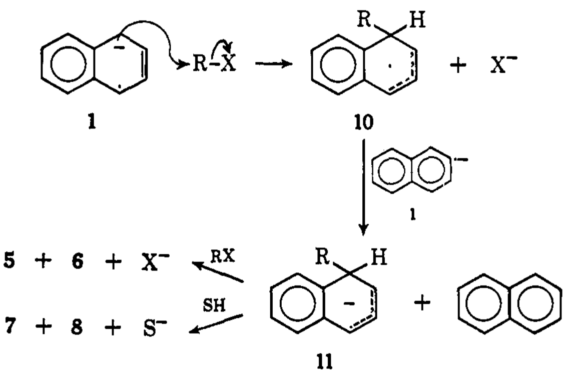
(5) Reaction of sodium anthracenide with simple alkyl halides yields products analogous to **5–9**: R. Gerdil and E. A. C. Lucken, *Helv. Chim. Acta*, **44**, 1966 (1961).



electron transfer from **1** to the alky halide.[2,6,7] Radical coupling yields **2**,[2] while electron transfer from **1** to R· produces a carbanionic moiety (R^-Na^+ or R–Na) which yields **3** by proton abstraction from solvent (SH).[6,7]



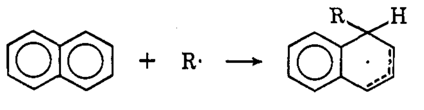
Two diverse mechanisms have been suggested to account for the formation of alkylation products (**5–9**). Lipkin[4a] postulates initial SN2 attack on the alkyl halide by a nucleophilic radical anion (**1**) (eq 1).



(1)

Subsequent reduction of the resulting free radical **10** yields a delocalized carbanion (**11**), which can attack another molecule of alkyl halide to yield products **5** and **6** or abstract a proton from solvent to form **7** and **8**.

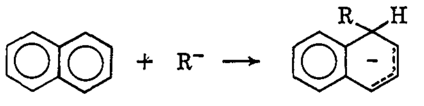
Hoijtink[8] suggests that alkylation is initiated by addition of an alkyl free radical to a molecule of naphthalene, which is produced in the charge-transfer reaction of **1** with the alkyl halide (2). The resulting delocalized free radical **10** is identical with the first intermediate postulated in eq 1, and subsequent steps in the alkylation reaction are common to both mechanisms.



(2)

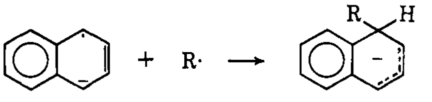
10

Two variations on the Hoijtink mechanism not previously proposed appear equally plausible. Alkylation might be initiated either by addition of an alkyl carbanion (R^-) to naphthalene (3) or by combination of an alkyl free radical and an aromatic radical anion (4). Both reactions lead directly to a delocalized carbanion (**11**) also common to the Lipkin mechanism.



(3)

11



(4)

1 11

We are now pleased to communicate the results of experiments which unequivocally establish eq 4 as a mechanism by which the formation of alkylation products is initiated. In addition, our data strongly suggest that eq 4 is the unique mechanism by which alkylation is initiated.

The displacement mechanism (eq 1) differs from the other three in that it requires that the ratio of aliphatic products (**2–4**) to alkylation products (**5–9**) be determined by competition between electron transfer and SN2 displacement during interaction of the alkyl halide with the radical anion **1**. This product partition ratio should thus be sensitive to structural variations in the alkyl halide which favor or disfavor one of these reactions relative to the other. The order primary > secondary > tertiary is well established for the rates of SN2 displacement on alkyl halides of varying degree of substitution at the α carbon.[9] Data of Warhurst and coworkers,[10] as well as data obtained by us for the composition of aliphatic products derived from reaction of **1** with a mixture of primary and secondary alkyl iodides,[2] suggest that the rate of electron transfer from **1** to alkyl iodides is relatively insensitive to the structure of the alkyl iodide. Thus one clearly predicts that were the displacement mechanism (eq 1) operative, the ratio of aliphatic products to alkylation products should increase markedly as the halide employed is varied from primary to secondary to tertiary. The data presented in Table I clearly demonstrate that this expectation is not realized in fact.

The radical–radical anion combination mechanism (eq 4) also requires that the product partition ratio be determined by the relative rates of two competing reactions between identical reactants, since combination of radical anion (**1**) and alkyl free radical leads to alkylation while electron transfer from **1** to the free radical leads ultimately to simple alkane (**3**). Since free-radical combination reactions have monotonously low activation energies,[11] one would not expect the

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[6] J. F. Garst, W. Ayers, and R. C. Lamb, *J. Am. Chem. Soc.*, **88** 4260 (1966).

[7] S. J. Cristol and R. V. Barbour, *ibid.*, **88**, 4261 (1966).

[8] G. J. Hoijtink, *Chem. Ing. Tech.*, **35**, 333 (1963).

[9] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; *Chem. Rev.*, **56**, 571 (1956).

[10] D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **51**, 1375 (1955).

[11] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 108 (1961); A. F. Trotman-Dickenson, *Ann. Rept. Chem. Soc. London*, **55**, 41 (1958).

rate of the combination reaction to be markedly sensitive to the structure of the free radical. Carbanion stabilities appear to decrease in the series primary > secondary > tertiary,[12] and one might expect this trend to be reflected in a decreasing rate of electron transfer to free radical as the radical site becomes progressively more highly substituted. Thus, if the radical–radical anion combination mechanism (eq 4) is operative, one expects the ratio of aliphatic products to alkylation products to *decrease* as the halide employed is varied from primary to secondary to tertiary. This expectation is confirmed by experiment (Table I).

Table I. Product Distribution from the Reaction of Sodium Naphthalenide (**1**) with Alkyl Iodides (RI)[a]

	% yield from			
Products	$(CH_3)_3CCH_2I$	n-$C_5H_{11}I$	s-$C_5H_{11}I$	t-$C_5H_{11}I$
R–R (**2**)	72 (70)	46	22 (22)	3
R–H (**3**)	17 (17)	16	17 (17)	22
Alkene (**4**)		3	4 (4)[b] 9 (9)[c]	8[d] 6[e]
Total aliphatic (**2–4**)	89 (87)	65	52 (52)	39
Total alkylation (**5–9**)[f]	11 (13)	35	48 (48)	61
Aliphatic/alkylation	8.1 (6.7)	1.9	1.1 (1.1)	0.64
Dialkylation/monoalkylation[g]	~0	2.5	0.72	~0

[a] Reactions were carried out by injecting a solution *ca.* 1 *M* in **1** into solutions 1 *M* in RI or, in the cases for which yields are reported in parentheses, into solutions 1 *M* in RI and 1 *M* in naphthalene. Injection of a solution of **1** was continued until all the RI was consumed, as indicated by the persistence of the deep green color characteristic of **1**. Each reported yield is the average of the values obtained for at least three independent reactions. Yields are reproducible to at least ±5% of the value reported. [b] 1-Pentene. [c] 2-Pentene. [d] 2-Methyl-1-butene. [e] 2-Methyl-2-butene. [f] The yield of alkylation products is determined by difference from the yield of aliphatic products, which were analyzed by vapor phase chromatography by employing heptane as an internal standard. The assumption that all iodide not converted to aliphatic products is consumed in the alkylation process was verified by quantitative analysis of the alkylation products in selected control experiments. [g] This approximate comparison was obtained by comparing the area under the peaks with retention times characteristic of C_{20} hydrocarbons with that for those characteristic of C_{15} hydrocarbons.

If the mechanism outlined in either eq 2 or 3 were operative, the product partition ratio would be determined by competition among several reactions involving a variety of reactants, and its dependence on the structure of the alkyl halide employed would be difficult to predict. Both mechanisms require that the relative yield of alkylation product increase in the presence of excess naphthalene, however, since in both cases the reaction which initiates alkylation is first order in naphthalene. In fact, the product partition ratio is found to be wholly insensitive to the presence of excess naphthalene (Table I).

These considerations lead us to the conclusion that all products of the reaction of sodium naphthalenide with alkyl iodides derive from an initial electron-transfer reaction which yields an alkyl free radical. Alkylation products result from a subsequent combination of this alkyl free radical with a second aromatic radical anion.

The generality of the radical–radical anion combination mechanism is demonstrated by the behavior of neopentyl iodide (Table I). If for primary halides the displacement mechanism were operative, one would expect a marked reduction in the yield of alkylation products from reaction of **1** with this substrate, as compared to that obtained from unhindered primary iodides. Experiment reveals that only a slight decrease ensues. This decrease is anticipated by the radical–radical anion combination mechanism, which leads to the formation of the delocalized carbanion **11**. As both Lipkin[4a] and Hoijtink[8] suggest, this carbanion can either react with alkyl halide to yield **5** and **6** or with solvent to yield **7** and **8**. The former reaction will be more competitive with the latter when alkyl halides which are good S_N2 substrates are employed. This expectation is confirmed experimentally (Table I). Very little, if any, neopentyl iodide is consumed by reaction with **11**, while a significant fraction of the *n*-pentyl iodide undergoes this reaction. Since iodide consumed in this manner cannot give rise to aliphatic products, the ratio of aliphatic to alkylated products must perforce be less for the reaction of **1** with *n*-pentyl iodide than for the reaction with neopentyl iodide.

The mechanistic conclusions presented in this communication are supported in part by the results of Garst and coworkers,[13] who find that the ratio of aliphatic products to alkylation products obtained from reaction of **1** with a series of 5-hexenyl halides is insensitive to the nature of the halogen atom. This result, while most difficult to reconcile with the displacement mechanism (1), is predicted by the radical–radical anion combination mechanism.

When considered together, the data of Garst and coworkers[13] and those presented in this communication allow one to conclude that all alkyl halides, regardless of the nature of either the alkyl fragment or the halogen atom, react with **1** *via* initial electron transfer and yield alkylation products only as a result of radical–radical anion combination.

Acknowledgment. Support of this research by the National Science Foundation and the Mobil Oil Corporation, in the form of an unrestricted grant-in-aid, is gratefully acknowledged. G. A. L. thanks the National Science Foundation for a summer stipend under the Undergraduate Research Participation Program. We are grateful to Mr. James N. Cron for valuable experimental assistance during the initial stage of this investigation.

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(12) D. J. Cram, "Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(13) J. F. Garst, J. T. Barbas, and F. E. Barton, III, *J. Am. Chem. Soc.*, 90, 7159 (1968).

G. Dann Sargent, Glenn A. Lux
Department of Chemistry, Amherst College
Amherst, Massachusetts 01002

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Stereospecificity of Carbonium Ions Related to Solvation Factors[1]

Sir:

We wish to report a dramatic effect of lithium perchlorate on the products of chlorinolysis, in dry

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[1] Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corp.