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 SN2 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.

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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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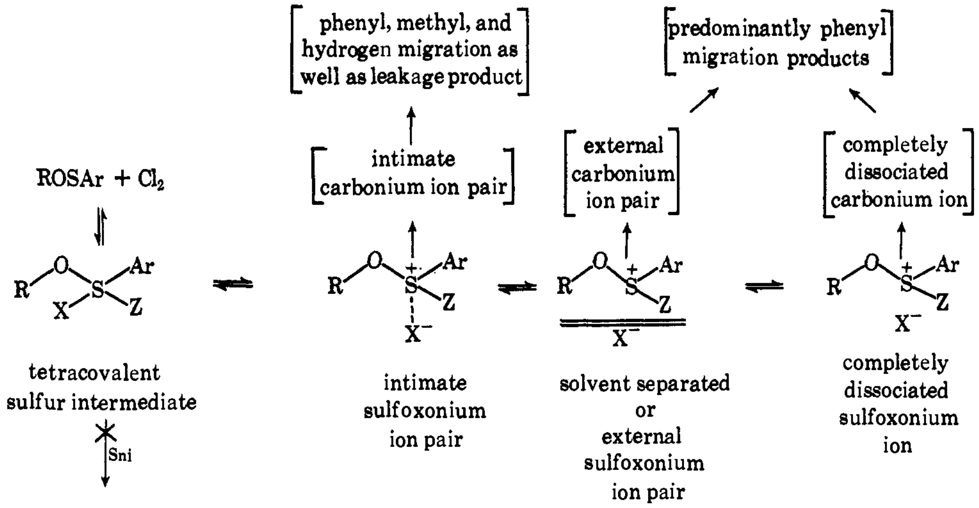
Scheme I. Product-Forming Pathways in Chlorinolysis of 3-Phenyl-2-butyl Sulfenate Ester[a]



[a] R = 3-phenyl-2-butyl, X = Cl, OAc, or ClO_4, and Z = Cl or OAc.

acetic acid, of the 2,4-dinitrobenzenesulfenate esters of *erythro*- and *threo*-3-phenyl-2-butanols (see Table I).

Table I. Summary of Products Obtained on Chlorinolysis of *erythro*- and *threo*-3-Phenyl-2-butyl 2,4-Dinitrobenzenesulfenates

	Products, %			
Reactant	Same[b] diastereomer	Combined products[d] of Me and H migration	Reciprocal of leakage[6] ratio[c]	Ratio chloride: acetate
D-*erythro*	70.9	22.8	11.3	3.0
L-*erythro*	72.2	21	10.5	2.7
DL-*erythro*[a]	80.9	14.8	24.5	0.8
L-*threo*	57.8	35.4	7.9	2.7
DL-*threo*[a]	72.8	20.7	17.8	0.8

[a] Contained 0.08 *M* $LiClO_4$ in acetic acid. [b] This column gives the total yield of *erythro* or *threo* acetate, chloride, and alcohol produced from *erythro* and *threo* reactant, respectively. [c] This column gives the ratio of *erythro* product (from *erythro* reactant) to *threo* product (first three runs) and the ratio of *threo* product (from *threo* reactant) to *erythro* product (last two runs).

This reaction involves the acetolysis of sulfoxonium ions[2] and proceeds under extremely mild conditions. The products are similar to those obtained during the deamination reaction;[3] their yields were determined by vapor phase chromatography and isotope dilution techniques using carbon-14.[4] In the chlorinolysis of α-phenylpropyl 2,4-dinitrobenzenesulfenate, several ion pairs were identified[2] with the help of the $LiClO_4$–LiCl criterion,[5] $LiClO_4$ hindering return from the external ion pair (see Scheme I).

The previous[2] results demonstrated the inheritance by the carbonium ion of a solvent cage organized originally about the ground-state sulfoxonium ions. A striking consequence of this effect is the increase of acetate produced at the expense of chloride. Thus the chloride is produced chiefly from intimate ion pairs, and acetate results from external ion pairs and other highly solvated cations. The same phenomena are observed in the cases reported here. The results given in the table show the effect of $LiClO_4$ in reducing total methyl and hydrogen migration in addition to partially suppressing leakage.[6] In other words, stereospecificity is increased as return from external ion pairs is retarded.

These results correlate well with the assumption that the extent and/or nature of the solvent environment of the carbonium ion strongly determines its stereospecific behavior. The product composition formed through the more stabilized solvent-separated (in contrast to tightly ion-paired) carbonium ion species evidently enjoyed in its lifetime a greater degree of freedom from leakage and was also less prone to suffer the comparatively unstable transition states involving methyl and hydrogen migrations. This conclusion also allows for the possibility that intrinsic structural features of the carbonium ion species may be regulated by solvation factors.

Finally, we must note the absence of any chloride product originating from the tetracovalent sulfur intermediate *via* an SNi process,[7] similar to that which gave rise to the alkyl chloride in chlorinolysis of the α-phenylpropyl sulfenate,[2] but this is not surprising. Cram[8] has analyzed and interpreted the absence of SNi products in the decomposition of the analogous 3-phenyl-2-butyl chlorosulfite. Very much the same reasoning may be applied again to account for the results being considered here.

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(5) Reference 3, pp 139–158.

(6) "Leakage" is the per cent crossover from *erythro* reaction to *threo* product or from *threo* reactant to *erythro* product during reaction.

(7) For example, an SNi process would produce L-*threo* chloride exclusively from L-*threo* sulfenate starting material. Such results were never obtained; only DL-*threo* chloride could be found.

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(9) Oak Ridge Associated Universities Predoctoral Fellow from the University of Delaware.