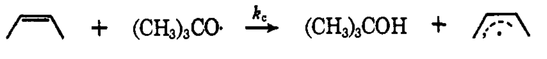
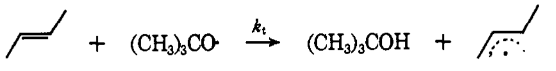


(2)

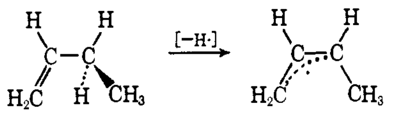
III



(3)

IV

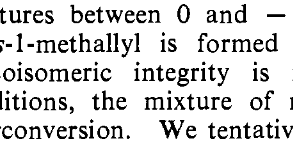
Examination of the esr spectra obtained from butene-1 shows the presence of only III and IV. The relative amounts of these isomeric radicals are temperature dependent (Figure 4). At relatively high temperatures between 0 and −100°, only slightly more *trans*-1-methallyl is formed than *cis* isomer. Since stereoisomeric integrity is maintained under these conditions, the mixture of radicals cannot arise by interconversion. We tentatively interpret the drop-off of the *trans* isomeric radical at temperatures less than −130° to an increased conformational preference of a *gauche* structure such as V for butene-1 at lower temperatures.[10–13] Further studies on steric effects are in progress.



V

(4)

The importance of the conformation of the reactant is shown further by the *addition* of *t*-butoxy radical to 1,3-butadiene. At −137° the esr spectrum of only the *trans* allylic radical VI is observed.[14] The coupling constants are highly consistent with the assignments for the other allylic radicals. The 1β and 3β hydrogens have degenerate coupling constants as in the analogous *trans* methallyl radical.



VI

coupling constants, G

$a_{1\alpha H} = 14.83$

$a_{1,3\beta H} = 13.74$

$a_{2H} = 3.88$

$a_{CH_2} = 16.97$

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(10) An examination of nmr coupling constants in butene-1 shows that the rotational conformers are about equally populated at ambient temperatures.[11] Recent calculations by N. L. Allinger, *et al.* [*J. Am. Chem. Soc.*, **90**, 5773 (1968)], indicate, however, that the *gauche* rotamer of butene-1 is 0.69 kcal/mol more stable than the *anti* form. Similarly, in propionaldehyde, a reasonable model, the *cis* rotamer is approximately 1 kcal/mol more stable than the *gauche* form, and the barrier to rotation is 2.3 kcal/mol.[12]

(11) A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(12) S. S. Butcher and E. B. Wilson, Jr., *J. Chem. Phys.*, **40**, 1671 (1964).

(13) A mixture of two isomeric 1-hydroxyallyl radicals was obtained from the photolysis of hydrogen peroxide in allyl alcohol by R. Livingston and H. Zeldes [*J. Chem. Phys.*, **44**, 1245 (1966)]. The relative concentrations of the isomers were temperature dependent, but they were unable to make structural assignments.

(14) The esr spectrum does not distinguish between VI and the oligomeric radicals resulting from further addition to butadiene. There is no doubt, however, that the configuration of all of these allylic radicals is *trans*. The broader lines observed in this case (*ca.* 0.5 G) may be due to either unresolved hyperfine interactions or a mixture of radicals.

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Radical Mechanism of Alkylation of Sodium Naphthalenide

Sir:

The potential competition between electron-transfer and nucleophilic displacement reactions is especially interesting for organic radical anions. In order to elucidate the factors which influence this competition, it is imperative that those reactions of radical anions which might proceed by either mechanism be correctly classified. Both pathways have been suggested for alkylations of sodium naphthalenide with alkyl halides. Data reported herein rule out the nucleophilic displacement mechanism for such alkylations with primary alkyl halides.

Reactions of sodium naphthalenide (:Naph·⁻) with alkyl halides (RX) in 1,2-dimethoxyethane (DME) lead to reduction products (RH)[1–3] and alkylation products.[4–6] The reduction products arise through successive electron-transfer reactions (eq 1–3).[1–3] Radical (eq 1 followed by eq 4) and S$_N$2 (eq 5) mechanisms have been suggested for the initial step of alkylation.[5,7] Subsequent alkylation probably proceeds from the anion which is the product in eq 6.[5]

$$:\mathrm{Naph}\cdot^- + \mathrm{RX} \longrightarrow :\mathrm{Naph} + \mathrm{R}\cdot + \mathrm{X}^- \quad (1)$$

$$:\mathrm{Naph}\cdot^- + \mathrm{R}\cdot \longrightarrow :\mathrm{Naph} + \mathrm{R}:^- \quad (2)$$

$$\mathrm{R}:^- \xrightarrow{\mathrm{DME}} \mathrm{RH} \quad (3)$$

$$:\mathrm{Naph} + \mathrm{R}\cdot \longrightarrow \cdot\mathrm{Naph\text{-}R} \quad (4)$$

$$\cdot\mathrm{Naph}:^- + \mathrm{RX} \longrightarrow \cdot\mathrm{Naph\text{-}R} + \mathrm{X}^- \quad (5)$$

$$\cdot\mathrm{Naph\text{-}R} + :\mathrm{Naph}\cdot^- \longrightarrow :\mathrm{Naph\text{-}R}^- + :\mathrm{Naph} \quad (6)$$

A direct answer to the question of the alkylation mechanism was sought by investigating the effects of halogen variation on the yields of reduction products, using primary (5-hexenyl) halides. Since the reduction and alkylation products are formed competitively, the yield of reduction product would vary from one halogen

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(1) (a) J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Am. Chem. Soc.*, **88**, 4260 (1966); (b) *Preprints, Div. Petrol. Chem.*, **13**, D65 (1968).

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

(3) J. F. Garst and F. E. Barton, II, unpublished work documenting the successive electron-transfer mechanism for production of 1-hexene and methylcyclopentane in reactions of 5-hexenyl fluoride with sodium naphthalenide in DME.

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

(5) D. Lipkin, F. R. Galiano, and R. W. Jordan, *Chem. Ind.* (London), 1657 (1963); see also D. Lipkin, G. J. Divis, and R. W. Jordan, *Preprints, Div. Petrol. Chem.*, **13**, D60 (1968), and further references therein.

(6) The alkylation products are principally dialkyldihydronaphthalenes and alkylnaphthalenes.[4,5]

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

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

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

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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[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).

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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).