1 H, $NHClO_3$, disappeared on addition of D_2O) and 1.32 ppm (s, 9 H, CH_3); ir (CCl_4) 3280 (m, NH), 1260 (s), 1210 (vs), 1020 (vs), and 660 cm^{-1} (s). The carbon tetrachloride solution underwent no visible or spectral changes within one week at ambient temperature.

An analytical sample was obtained by vacuum transfer to a $-78°$ receiver at 0.02 mm.

Anal. Calcd for $C_4H_{10}NClO_3$: C, 30.86; H, 6.46; Cl, 22.87. Found: C, 29.62; H, 6.47; Cl, 22.62.

Potentiometric titration gave an equivalent weight of 151 ± 4 (calcd 155) and an ionization constant of 1.51×10^{-7}.

***N*-Perchlorylhexylamine.** The above procedure gave a 63% yield of *N*-perchlorylhexylamine: nmr (CCl_4) δ 6.73 (broad t, 1 H, $NHClO_3$, disappeared on addition of D_2O), 3.42 (q, 2 H, CH_2N), 1.40 (m, 8 H, CH_2CH_2), and 0.93 ppm (distorted t, 3 H, CH_3); ir (CCl_4) 3290 (w, OH), 1240 (sh), 1210 (vs), 1020 (s), and 665 cm^{-1} (s). On standing at ambient temperature for 3 days, the compound was completely converted to hexanoic acid and an unidentified inorganic solid. Hexanoic acid was identified by ir, nmr, and glpc comparison with an authentic sample.

***N*-Perchlorylpropylamine.** The above procedure gave *N*-perchlorylpropylamine in 61% yield: nmr (CCl_4) δ 6.9 (broad, 1 H, $NHClO_3$), 3.4 (m, 2 H, CH_2N), 1.72 (m, 2 H, CH_2CH_3), and 1.07 ppm (t, J = 6 Hz, CH_3); ir (CCl_4) 3270 (m, NH), 1250 (s), 1240 (sh), 1210 (vs), 1030 (vs), and 645 cm^{-1} (s). The compound was completely converted in 18 hr at ambient temperature to propionic acid and an unidentified inorganic material.

***N*-Perchlorylisopropylamine.** The above procedure gave *N*-perchlorylisopropylamine in 60% yield: nmr (CCl_4) δ 6.7 (broad, 1 H, $NHClO_3$), 3.83 (m, 1 H, CH), and 1.33 ppm (d, J = 7 Hz, CH_3); ir (CCl_4) 3270 (m, NH), 1230 (sh), 1205 (vs), 1020 (vs), and 660 cm^{-1} (s). The compound in carbon tetrachloride was 60% converted to acetone in 1 week.

Sodium Salts of *N*-Perchloryl Primary Amines. Extracting the carbon tetrachloride solutions of *N*-perchloryl primary amines with 1 *N* sodium hydroxide left nothing in the carbon tetrachloride layer observable by nmr. Acidification of the aqueous layer resulted in reextraction of the starting material with no change in nmr and in ir spectra.

***N*-Chloro-*N*-perchlorylhexylamine.** A solution of 0.95 mmol of *N*-perchlorylhexylamine in 5 ml of carbon tetrachloride was stirred for 5 min with 5 ml of 5% aqueous sodium hypochlorite, and the organic layer was dried. Nmr and ir spectra of the solution showed no evidence of NH, and the product was not affected by extraction with 1 *N* sodium hydroxide. Analysis by nmr using chlorobenzene as a quantitative reference indicated an 87% yield of *N*-chloro-*N*-perchlorylhexylamine: nmr (CCl_4) δ 3.70 (t, J = 6 Hz, 2 H, CH_2N), 1.40 (broad m, 8 H, $-CH_2-$), and 0.90 ppm (distorted t, 3 H, CH_3); ir (CCl_4) 1250 (vs), 1220 (vs), 1020 (s), 975 (m), and 650 cm^{-1} (m). The compound in carbon tetrachloride was completely converted to hexanoic acid in 20 hr.

***N*-Chloro-*N*-perchlorylbutylamine.** By the above procedure, 0.92 mmol of *N*-perchlorylbutylamine in 5 ml of carbon tetrachloride gave an 84% yield of *N*-chloro-*N*-perchlorylbutylamine: nmr (CCl_4) δ 3.65 (t, J = 6 Hz, 2 H, CH_2N), 1.7 (broad m, 4 H, CH_2), and 1.0 ppm (distorted t, 3 H, CH_3); ir (CCl_4) 1250 (vs), 1220 (vs), 1020 (vs), and 650 cm^{-1} (s).

Reactions of 1,4- and 1,5-Dihaloalkanes with Alkali Naphthalenes[1,2]

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Abstract: Reactions of 1,4-dihalobutanes and 1,5-dihalopentanes with alkali naphthalenes give reduction products (mostly cycloalkanes and olefins) and alkylation products (alkylated naphthalene derivatives). The products do not include dimeric or polymeric residues of the dihaloalkanes. Thus, initially formed alkyl radicals do not couple. Instead, they react with alkali naphthalene to give alkyl and alkylated naphthalene anions. Therefore, alkyl dimers from reactions of monoiodoalkanes with sodium naphthalene cannot arise from coupling of initially formed radicals. They must result instead from reactions of alkyl anions, probably with alkyl iodides. These are not conventional SN2 reactions; they may involve intermediate radical pairs. From the fact that the reduction–alkylation ratio from the α,ω-dihaloalkanes is halogen and chain length independent it is concluded that the intermediate ω-haloalkyl radicals are not bridged and that they do not undergo internal SH reactions. No definitive conclusions can be reached on the mechanisms of the reactions of intermediate ω-haloalkylalkalies to give cycloalkanes and olefins. For the iodides, it appears that the postulate of intermediate α,ω-alkadiyls (diradicals) is consistent with available data, but for other halogens this is not easily reconciled with the fact that there is a substantial halogen effect on the distribution among the resulting cycloalkanes and olefins.

Studies of reactions of monohaloalkanes with sodium naphthalene and related compounds in DME and other ethers have led to Scheme I.[2-4] The least understood aspect of these reactions has persisted in being the route to alkyl dimers, which dominate when alkyl iodides are reactants. We initiated studies of reactions of 1,4-diiodobutane with sodium naphthalene in order to test one of the theories of alkyl dimer formation that had been proposed earlier. The results are germane to additional topics of interest, and the studies were expanded to include other α,ω-dihaloalkanes and some variations in the alkali arene and the solvent. Here we consider reactions of 1,4-dihalobutanes and 1,5-dihalopentanes.

Experimental Section

Solvents. 1,2-Dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MeTHF) were refluxed over fresh-cut sodium for 12 hr then fractionally distilled on a spinning band

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

(2) Part of this work has been published in preliminary form: (a) J. F. Garst and J. T. Barbas, *J. Amer. Chem. Soc.*, **91**, 3385 (1969); (b) *Tetrahedron Lett.*, 3125 (1969).

(3) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969).

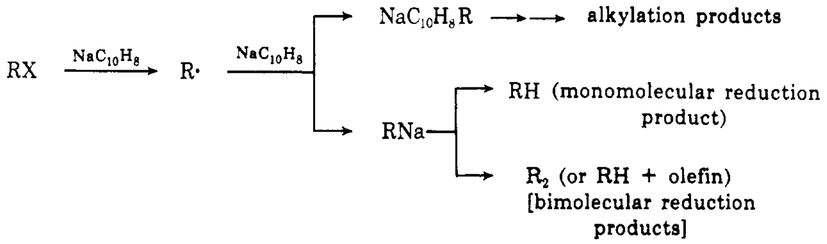
(4) The foundations of Scheme I have been reviewed recently from several viewpoints.[5-7]

(5) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).

(6) J. F. Garst, "Free Radicals," J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, pp 520–527.

(7) J. F. Garst, "Chemically Induced Magnetic Polarization," A. R. Lepley and G. L. Closs, Ed., Wiley, New York, N. Y., 1973, p 223 ff.

Scheme I



column. Purity was tested by vpc to ensure that there were no low-boiling components which might interfere with analyses. The solvents were degassed and stored over sodium benzophenone–disodium benzophenone in a reservoir on the vacuum manifold.

Purification of Alkyl Halides. Alkyl halides were fractionally distilled on an annular Teflon spinning band column. For high-boiling iodides and diiodides, reduced pressures were used to avoid decomposition. Iodides were filtered through neutral alumina. Immediately before use, halides were collected from vapor phase chromatography on 0.25-in. columns in a Varian Aerograph Model 1200-1 Hi Fi III instrument. The following columns were used: (1) 0.25 in. × 10 ft 20% QF-1 on 60–80 Chromosorb W-DMCS treated; (2) 0.25 in. × 10 ft 10% 8N8 Flexol Plasticizer on 60–80 Chromosorb W-DMCS treated; (3) 0.25 in. × 10 ft 10 in. SF-96 on 60–80 Chromosorb W-DMCS treated. The pure alkyl halides were then degassed on the vacuum manifold. Syringes were flushed with nitrogen before these halides were withdrawn to be injected into radical anion solutions.

Preparations of Alkyl Halides. Except for 1,5-diiodopentane, tetrahydrofurfuryl iodide, and tetrahydrofurfuran bromide, all alkyl halides were obtained commercially, then purified as described above.

1,5-Diiodopentane was prepared by the reaction of HI with tetrahydropyran. Orthophosphoric acid (85%, 150.5 g, 1.0 mol) and phosphoric anhydride (32.5 g) were placed in a 1-l. three-necked flask fitted with a stirrer, a reflux condenser, and a thermometer. With cooling and stirring, KI (166 g, 1.0 mol) then tetrahydropyran (43 g, 0.5 mol) were added slowly. The mixture was heated to reflux for 3 hr. After cooling to room temperature, diethyl ether (125 ml) was added. The solution was filtered and decolorized with a 10% sodium thiosulfate solution, then the ether layer was separated and washed with cold saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. Following evaporation of the ether, the residue was distilled under reduced pressure, the fraction boiling at 142–143° (16 Torr) being collected. This was redistilled on an annular Teflon spinning band column, the fraction boiling at 86° at 0.9 Torr being taken: yield 82%; nmr (CCl_4) 3.15 (t, 4 H), 1.95 (m, 4 H), 1.62 ppm (m, 2 H); mass spectrum parent ion peak at *m/e* 324.

Tetrahydrofurfuryl bromide was prepared from tetrahydrofurfuryl alcohol by a modification of a literature procedure.[8] To 96 g (0.36 mol) of freshly distilled PBr_3 and 50 ml of ether was added 15 g of dry pyridine over 20 min. After cooling to −20° with an ice–methanol bath, a mixture of 102 g (1.0 mol) of tetrahydrofurfuryl alcohol and 5 g of dry pyridine was added slowly with stirring and cooling over 4 hr, after which followed 1 hr of further stirring at −20° before the reaction mixture was allowed to warm to room temperature and stand for 36 hr. The ether was removed and the residue distilled, the fraction boiling 69–70° (22 Torr) being retained. Further distillation on an annular Teflon still, collecting the fraction boiling at 49–50° (4 Torr), led to a 65% yield of tetrahydrofurfuryl bromide.

Tetrahydrofurfuryl iodide was prepared from the bromide by its overnight reaction with excess sodium iodide in dry acetone (stirred). The dark red reaction mixture was decolorized by several filtrations through neutral alumina, the acetone was removed on a rotary evaporator, and the tetrahydrofurfuryl iodide was collected as needed from vapor phase chromatography on a 0.25 in. × 5 ft 10% 8N8 Flexol Plasticizer column at 130°. The yield was not determined, since the iodide was not isolated at one time. It decomposes on standing at room temperature: ir 2960, 2860, 1060 cm^{-1}; nmr (CCl_4) 3.15 (2 H), 3.85 (m, 3 H), 1.90 ppm (m, 4 H); mass spectrum parent ion peak at *m/e* 212.

Reactions. Special reaction vessels (Pyrex) consisted of a 10-ml calibrated test tube connected at the top to a constricted arm having a 10/30 inner joint at its end. Near the top of the test tube were attached four other side arms. One led to a short 11-mm side tube (for storage of naphthalene), a second led to a quartz optical cell, the third was equipped with a coarse fritted disk beyond which was a vertical tube with several constrictions (for preparation of sodium mirrors and their reactions with naphthalene), and the fourth was a short arm leading directly into the main body of the assembly (for injections of the alkyl halide through a serum cap).

Naphthalene (0.3 to 1.0 g) was placed in the side tube which in turn was closed with a serum cap. A piece of sodium was sealed into the chamber of the mirror tube most remote from the main body of the vessel. Through the 10/30 joint, the whole assembly was attached to the vacuum manifold and flamed under vacuum. The sodium was successively distilled, using a weak flame, through the constrictions until a fine reactive mirror deposited between the two constrictions nearest the main body, after which the more remote portion of the mirror tube was cut off with the torch. The solvent was distilled from the storage reservoir to the main body of the vessel by cooling the latter in liquid nitrogen. At a constriction below the 10/30 joint, the vessel was sealed off from the vacuum manifold and the solvent allowed to reach room temperature by spraying the vessel with acetone. This procedure seemed to minimize cracking of the main vessel, which sometimes happened during warm-up. The naphthalene was dissolved in the solvent and the vessel tilted to allow the solution to flow through the fritted disk and contact the sodium mirror. When the desired concentration of sodium naphthalene (determined by optical density) had been attained, the solution was filtered back through the disk into the main body, frozen in liquid nitrogen, and permanently separated from the sodium mirror by cutting off the mirror tube. At 8200 Å, the extinction coefficient of sodium naphthalene in DME is 2500. In the experiments reported here, these concentrations were always between 10^{-2} and 10^{-1} *M*, and no concentration effects on product distributions were noted. The desired quantity of alkyl halide was weighed in a hypodermic syringe and injected directly into the sodium naphthalene solution with vigorous shaking. Alkyl halide less than and greater than equivalent to the alkali naphthalene was used, with no detected effects on products. Finally, the solution was quenched with glacial acetic acid and nitrogen admitted into the reaction vessel until the pressure was 1 atm. The reactions occur instantaneously (on a laboratory time scale) on mixing the reactants.

One variation of the above procedure involved the other order of injection, that is, sodium naphthalene solution prepared as above was injected into an alkyl halide solution until the color of sodium naphthalene persisted.

Another variation employed evaporation to mix the reagents. Sodium naphthalene was prepared as previously described in a reaction vessel with a 50-ml round-bottomed flask for the main body. The alkyl halide was placed in a side arm and heated to 35–45°, so that the alkyl halide slowly vaporized and deposited in the stirred, concentrated (*ca.* 0.1 *M*) solution of sodium naphthalene at 25°. "Evaporation" experiments were designed to avoid mixing problems as well as to suppress dimer formation and dialkylation products.

For experiments with lithium naphthalene, a lithium mirror was created by distilling ammonia from a solution of lithium in liquid ammonia. For cesium naphthalene, cesium mirrors were deposited by distilling cesium from a mixture of cesium chloride and calcium metal. Otherwise, the procedures for reactions of sodium naphthalene were followed.

Product Analyses. Quantitative product analyses were done by vpc using a Varian Aerograph Model 1200-1 Hi Fi III flame ionization detection instrument and internal standards. Peak areas were determined by disk integration, digital integration, or integration by cutting and weighing peak traces, with frequent cross checks among the three methods. Peaks were assigned by com-

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[8] L. H. Smith, "Organic Syntheses," Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1955, p 793.

Table I. Yields of Reduction Products from Reactions of Primary Alkyl Halides with Sodium Naphthalene in DME[a]

Expt	Alkyl halide	Yield reduction products	Reduction products
117	5-Hexenyl iodide	41%[b]	1-Hexene, methylcyclopentane
115	5-Hexenyl bromide	47[c]	1-Hexene, methylcyclopentane
108	5-Hexenyl chloride	55	1-Hexene, methylcyclopentane
193[d]	5-Hexenyl fluoride	58	1-Hexene, methylcyclopentane
167	1,4-Diiodobutane	55 (44%)[e]	Cyclobutane, ethylene
175	1,4-Diiodobutane	54 (−78°)	Cyclobutane, ethylene
176	1,4-Diiodobutane	57 (−50°)	Cyclobutane, ethylene
174	1,4-Dibromobutane	58	Cyclobutane, ethylene
203	1,4-Dichlorobutane	59	Cyclobutane, ethylene
201	1,5-Diiodopentane	57 (50%)[e]	Cyclopentane, 1-pentene
212	1,5-Dibromopentane	57	Cyclopentane, 1-pentene, pentane
210	1,5-Dichloropentane	63	Cyclopentane, 1-pentene, pentane

[a] Unless otherwise noted reactions were at room temperature. [b] "Evaporation" experiment. Monomolecular reduction products were accompanied by 7% bimolecular reduction not included above. Some dialkylation products were also probably formed. [c] "Evaporation" experiment. Accompanied by 5% bimolecular reduction products. [d] From the dissertation of F. E. Barton, II, The University of Georgia, 1969. [e] Values in parentheses are the yields of alkylation products directly determined by vpc.

parisons with authentic samples which were added to the reaction mixtures, using several different columns. In many cases, samples were trapped from the vpc using a splitter sending 90% of the effluent gases around the detector. Both nmr and mass spectra were obtained for trapped materials, and the spectra were compared with those of authentic samples. In other cases, gases separated by vpc were led directly from the vpc into the mass spectrometer. When authentic materials added to reaction mixtures produced new peaks in the vpc traces, it was considered established that those materials were not reaction products.

Analyses for C_4 and C_5 hydrocarbons from reactions of 1,4- and 1,5-dihaloalkanes employed a $^1/_8$ in. × 12 ft Porapak-S column of 80–100 mesh at 170° and a $^1/_8$ in. × 24 ft 10% silver nitrate–propylene glycol column at 50°. Both columns separated cleanly cyclobutane, 1-butene, 1,3-butadiene, butane, ethylene, cyclopentane, 1-pentene, 1,5-pentadiene, pentane, methyl vinyl ether, and methanol. For the C_4 hydrocarbons, the internal standard was pentane; for the C_5 hydrocarbons, it was cyclopentene.

Analyses for C_8 and C_{10} hydrocarbons used a $^1/_8$ in. × 12 ft 20% polyphenyl ether (five-ring) column at 140°.

Alkylated dihydronaphthalenes were analyzed at 130° on a $^1/_8$ in. × 6 ft 20% QF-1 column on 60–80 Chromosorb W-DMCS treated. For the C_{14} compounds 9-methylfluorene was the internal standard; the latter compound also served for the C_{15} hydrocarbons, but bibenzyl was sometimes used as an alternative.

Flame detector response factors were determined for all compounds for which authentic samples were available. For the C_{14} and C_{15} alkylation products, the response factors were assumed to be the same (per gram) as the internal standards. This assumption is justified by the findings of Dietz.[9]

Results and Discussion

Mechanism of Alkyl Dimer Formation. Up to 70% yields of alkyl dimers result from reactions of simple alkyl iodides with sodium naphthalene in DME,[10] but bromides give much less and chlorides and fluorides essentially none.[5–7] Sargent, Cron, and Bank proposed that alkyl dimers result from coupling of initially formed alkyl radicals (Scheme II),[10] but Garst and

Scheme II

$$\mathrm{RI} \xrightarrow{\mathrm{NaC_{10}H_8}} \mathrm{R}\cdot \xrightarrow{\mathrm{R}\cdot} \mathrm{R_2}\ (\text{or RH + olefin})$$

Barbas[2b] and Bank and Bank[3] have challenged this view, favoring Scheme I instead. Since arguments based on some of the present data have been given in a preliminary report[2b] and in reviews,[5–7] only a skeletal exposition is necessary here.

The main argument is simply that if Scheme II is operative, then intermediate 4-iodobutyl and 5-iodopentyl radicals should dimerize in reactions of 1,4-diiodobutane and 1,5-diiodopentane with sodium naphthalene. They do not. No C_8 or C_{10} hydrocarbons (except naphthalene) are formed. Cyclobutane, ethylene, and C_{14} alkylation products account quantitatively for the 1,4-diiodobutane consumed (Table I, experiment 167), and cyclopentane, 1-pentene, and C_{15} alkylation products similarly account for 1,5-diiodopentane (Table I, experiment 201). These product distributions are insensitive to the order of mixing reactants, and "evaporation" experiments (see Experimental Section) give the same product distributions as injection experiments.

The data of Table I are consistent instead with Schemes I and III, the latter being a version of Scheme I specialized for reactions of dihaloalkanes. The halogen-independent reduction–alkylation product partitioning is satisfied by the competing radical combination and electron transfer reactions of R· and $X(CH_2)_{n-1}CH_2\cdot$ with sodium naphthalene in Schemes I and III. The finding of ~58% reduction products in each reaction and the demonstrations that the reduction–alkylation product balance is essentially quantitative imply that intermediate ω-haloalkyl radicals and 5-hexenyl radicals are all partitioned alike in their reactions with sodium naphthalene, ~58% electron transfer (leading to reduction products) and ~42% radical combination (leading to alkylation products). C_8 and C_{10} hydrocarbons do not result from reactions according to Scheme III because the intramolecular reactions of 4-halobutylsodiums and 5-halopentylsodiums are much faster than their analogous intermolecular reactions.

The facts that ~83% yields of 4-penten-1-ol are formed in reactions of tetrahydrofurfuryl iodide, bromide, and chloride and that no tetrahydrofurfuryl dimer was detected argue similarly against Scheme II. Dimer formation through the route of Scheme I is subverted by the rapid opening of tetrahydrofurfuryl anions to 4-penten-1-oxide ions.

Other evidence against Scheme II comes from CIDNP and anion trapping experiments.[3,5–7]

Upper Limit of Internal SH Reactions of ω-Haloalkyl Radicals. Internal SH reactions are a possible route to cyclic hydrocarbons (eq 1). If they occurred in

$$X(CH_2)_{n-1}CH_2\cdot \longrightarrow \text{cyclo}(CH_2)_n + X\cdot \qquad (1)$$

reactions of α,ω-dihaloalkanes with sodium naphthalene,

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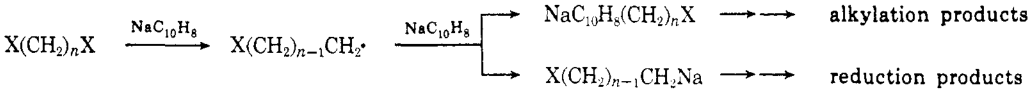
(9) W. A. Dietz, *J. Gas Chromatogr.*, **5**, 68 (1967).

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

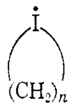
Scheme III



$$\begin{tikzcd} X(CH_2)_nX \arrow[r, "NaC_{10}H_8"] & X(CH_2)_{n-1}CH_2\cdot \arrow[r, "NaC_{10}H_8"] \arrow[dr] & NaC_{10}H_8(CH_2)_nX \arrow[r, "\longrightarrow"] & \text{alkylation products} \\ & & X(CH_2)_{n-1}CH_2Na \arrow[r, "\longrightarrow"] & \text{reduction products} \end{tikzcd}$$

they would be an additional source of cycloalkane, which would cause the yields of reduction products (including cycloalkanes) to rise above 58%, which is not observed. Assuming that more than a 10% increase in reduction product yield could have been detected, taking the rate constant for reactions of primary alkyl radicals with sodium naphthalene to be $\sim 2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$, and using our lowest initial concentration of sodium naphthalene ($\sim 10^{-2}\ M$), we estimate an upper limit of $\sim 3 \times 10^6\ \text{sec}^{-1}$ for the rate constant for the internal S_H reactions of 4-iodobutyl and the other intermediate ω-haloalkyl radicals in our reactions. It should be noted that the estimated rate constant for the internal S_H reaction of 3-iodopropyl is only $\sim 2 \times 10^3\ \text{sec}^{-1}$ at 111°.[11]

Bridging in ω-Haloalkyl Radicals. We rule out Scheme II because ω-iodoalkyl radicals from 1,4-diiodobutane and 1,5-diiodopentane do not couple. This argument assumes that these radicals behave just as typical primary alkyl radicals. A conceivable alternative is that the ω-iodoalkyl radicals do not behave as typical primary alkyl radicals; perhaps they are bridged (**1**), and perhaps the bridged radicals are less prone to couple than typical primary alkyl radicals.



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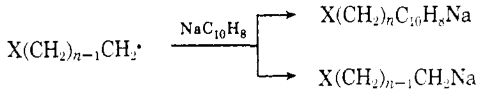
This combination of circumstances seems remote indeed in view of the facts that the reduction–alkylation product distribution is absolutely typical for reactions of 1,4-diiodobutane and 1,5-diiodopentane and that this distribution is independent of the nature of the halogen and the chain length in the α,ω-dihaloalkane reactions. If bridging occurs, it has no effect on the partitioning in the reactions of the ω-haloalkyl radicals with sodium naphthalene. In view of the fact that this partitioning does respond to other variations in radical structure (tertiary radicals suffer relatively more coupling than primary radicals;[12] tetrahydrofurfuryl radicals suffer relatively more reduction, consistent with an increased electron affinity due to the inductive effect of the oxygen), some effect of bridging would be expected, probably increased reduction, due to the participation of the electronegative halogen. Thus, we conclude that the ω-haloalkyl radicals are very unlikely to be bridged.[13,14]

Rate enhancements have been attributed to participation by remote halogens in some reactions, *e.g.*, reactions of alkyl iodides with $Co(CN)_5^{3-}$,[15] but we prefer to regard these as inductive effects or "through-bond" interactions involving orbital mechanisms similar to those discussed by Hoffmann.[16]

Mode of Reaction of ω-Haloalkyl Radicals with Electron Sources. In principle, ω-haloalkyl radicals can react with sodium naphthalene according to eq 2 as well as eq 3.

$$XCH_2(CH_2)_{n-2}CH_2\cdot \xrightarrow{NaC_{10}H_8} \cdot CH_2(CH_2)_{n-2}CH_2\cdot \quad (2)$$



$$\begin{tikzcd} X(CH_2)_{n-1}CH_2\cdot \arrow[r, "NaC_{10}H_8"] \arrow[dr] & X(CH_2)_nC_{10}H_8Na \\ & X(CH_2)_{n-1}CH_2Na \end{tikzcd} \quad (3)$$

If the diradicals formed by reaction 2 were to undergo such rapid unimolecular reactions that they are not scavenged by sodium naphthalene, then reaction 2 would provide a route to cycloalkanes and olefins in addition to that of reaction 3 (and Scheme III). This would have led to deviations from the "normal" 58% yields of reduction products, and such deviations are not observed. Either the α,ω-alkadiyls (diradicals) are nearly completely scavenged by sodium naphthalene (with the same radical combination–electron transfer ratio as primary alkyl radicals) or reaction 2 is not significant. The rate constants for reactions of sodium naphthalene ion pairs in DME with butyl halides have been determined recently: $k_{BuCl} \simeq 10^2\ M^{-1}\ \text{sec}^{-1}$; $k_{BuBr} \simeq 10^5\ M^{-1}\ \text{sec}^{-1}$; $k_{BuI} \simeq 10^8\ M^{-1}\ \text{sec}^{-1}$.[17,18] The rate constant for the reaction of 5-hexenyl radicals with sodium naphthalene in DME has been estimated as $\sim 2 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.[19] If these values are assumed for reactions 2 and 3 it is concluded that reaction 2 cannot compete with reaction 3 for X = Br or Cl, but for X = I about 5% of the reaction is predicted to proceed through reaction 2. We cannot claim that our product analyses are sufficiently precise to rule out this level of reaction 2, but we do believe that we would have detected as little as a 10% increase in the yields of reduction products due to the incursion of reaction 2.

The gas phase reactions of α,ω-dihaloalkanes with alkali metal atoms have been interpreted in terms of reactions 4 and 5 (an analog of reaction 2) instead of

$$XCH_2(CH_2)_{n-2}CH_2X \xrightarrow{M} XCH_2(CH_2)_{n-2}CH_2\cdot + MX \quad (4)$$

$$XCH_2(CH_2)_{n-2}CH_2\cdot \xrightarrow{M} \cdot CH_2(CH_2)_{n-2}CH_2\cdot + MX \quad (5)$$

reactions 4 and 6 (an analog of the lower branch of

$$XCH_2(CH_2)_{n-2}CH_2\cdot \xrightarrow{M} XCH_2(CH_2)_{n-2}CH_2M \quad (6)$$

reactions 3).[20-23] Reaction 6, with the ω-haloalky-

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(11) R. F. Drury and L. Kaplan, *J. Amer. Chem. Soc.*, **95**, 2217 (1973).

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

(13) L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N. Y., 1972; see pp 302 and 303 for a skeptical assessment of the argument given here.

(14) W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967). These authors find no evidence for bridging or internal S_H reactions in the 5-bromopentyl radical.

(15) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 582 (1969).

(16) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

(17) D. Juckett and S. Bank, paper presented at the First Fall Organic Conference, N. Falmouth (Cape Cod), Mass., Oct., 1973.

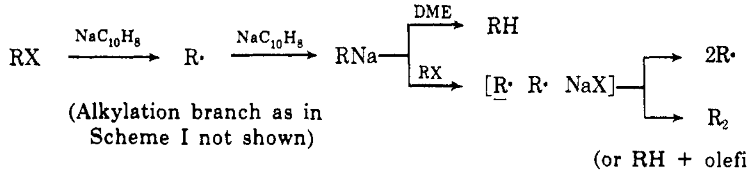
(18) B. Bockrath and L. M. Dorfman, *J. Phys. Chem.*, **77**, 2618 (1973).

(19) J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969); *J. Amer. Chem. Soc.*, **96**, 523 (1974).

(20) (a) C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, **34**, 608 (1938); (b) C. E. H. Bawn and W. J. Dunning, *ibid.*, **35**, 185 (1939); (c) C. E. H. Bawn and J. Milsted, *ibid.*, **35**, 889 (1939).

(21) P. S. Skell, E. J. Goldstein, R. J. Petersen, and G. L. Tingey, *Ber.*, **100**, 1442 (1967).

Scheme IV



alkali going on to the observed cycloalkane and olefin products, also seems tenable.

Further Aspects of the Mechanism of Alkyl Dimer Formation. Strong evidence has been accumulated that the alkyl dimers do not arise through coupling of initially formed alkyl radicals (Scheme II) or through nucleophilic displacements of alkyl anions (alkysodiums) on alkyl iodides, at least, not displacements which are subject to the usual effects found for SN2-E2 reactions.[10,12] Then what is the mechanism of dimer formation?

The next most likely mechanism parallels that invoked for reactions of alkyllithiums with alkyl halides in some circumstances (Scheme IV). Scheme IV is a particular formulation of Scheme I in which the conversion of RNa to R_2 is spelled out in mechanistic detail. It invokes the geminate radical pair formation that has become familiar through many recent reports involving CIDNP from alkyllithium–alkyl halide reactions.[24] It can be presumed that the "back-side attack" and steric requirements operative in conventional SN2 reactions do not play a role in these processes, so that formation of dimers from tertiary and neopentyl systems is not inhibited by these factors.

Sargent and Lux have reported the yields of R_2 and olefin from reactions of a series of pentyl iodides with sodium naphthalene in DME.[12] Sheldon and Kochi have reported similar data for peroxide photolyses in pentane at 30°.[25] If Scheme IV is correct, the two sets of data should provide bases for computing similar rate constant ratios for radical disproportionation (k_d) and combination (k_c). Table II gives appropriate comparisons for primary, secondary, and tertiary radicals. The agreement is good. However, a troubling point is noted in the following section.

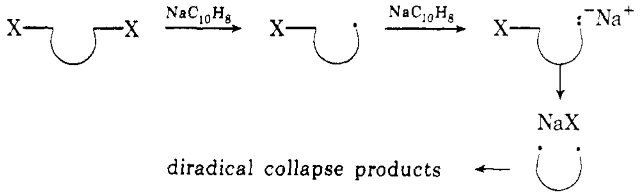
Table II. Radical Disproportionation–Combination Ratios Derived from Photolyses of Peroxides in Pentane at 30° and from Reactions of Alkyl Iodides with Sodium Naphthalene in DME at Room Temperature

Radical	k_d/k_c[a]	(Reaction)
n-Butyl	0.07	(Peroxide)[b]
n-Pentyl	0.065	(RI–$NaC_{10}H_8$)[c]
sec-Butyl	0.20	(Peroxide)[b]
sec-Pentyl	0.24	(RI–$NaC_{10}H_8$)[c]
tert-Butyl	0.80	(Peroxide)[b]
tert-Pentyl	1.2	(RI–$NaC_{10}H_8$)[c]

[a] The rate constant for disproportionation k_d is normalized by dividing the total disproportionation rate constant by the number of hydrogen atoms available for transfer in the disproportionation reaction. [b] From ref 25. [c] From ref 12.

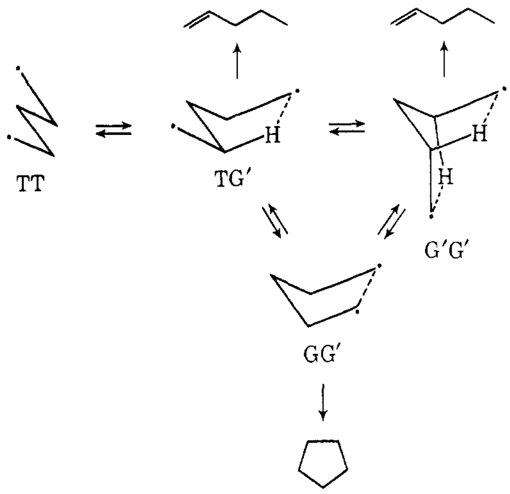
Cycloalkane and Olefin Formation for α,ω-Dihaloalkanes. Scheme V is a specialized version of Scheme IV. It implies that distributions among reduction products, which would be products of diradical collapse, might be independent of the nature of the halogen and metal. This is found for gas phase reactions of α,ω-dihaloalkanes with alkali metals, but it is definitely not the case for reactions of the same α,ω-dihaloalkanes with alkali naphthalenes in DME. The products are most sensitive to the halogen, and the effect is most clearly demonstrated by the data for the 1,5-dihalopentanes (Table III), for which the ratio cyclopentane/1-pentene varies as follows: I, 2.8; Br, 23; Cl, >100.

Scheme V



If Scheme V applies for all halogens, then the diradical intermediates must somehow differ (they cannot be the "same") as the halogen is varied. Scheme VI illustrates the various pentane-like conformations of 1,5-pentadiyl. Conceivably, differences in initial diradical conformations, as the halogen is varied, could provide a basis for the halogen effect on the product distribution, since conformational interconversions may be slow compared to, or competitive with, diradical collapse (from the electronic singlet). Inspection of space filling models did not reveal an obvious basis for acceptance or rejection of this hypothesis.

Scheme VI



α,ω-Alkadiyls formed in gas phase singlet sensitizations of cyclohexanone and cyclopentanone give much more olefin than cycloalkane, in contrast to the reactions

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(22) R. J. Petersen, Ph.D. Dissertation, The Pennsylvania State University, 1964.

(23) E. J. Goldstein, Ph.D. Dissertation, The Pennsylvania State University, 1964.

(24) A recent review is given by H. Ward, R. G. Lawler, and R. A. Cooper, ref 7, p 281 ff.

(25) R. A. Sheldon and J. K. Kochi, *J. Amer. Chem. Soc.*, **92**, 4395 (1970).

Table III. Distributions of Reduction Products from Reactions of 1,4-Dihalobutanes and 1,5-Dihalopentanes with Sodium Naphthalene in DME at Room Temperature[a]

Expts	Alkyl halide	Cycloalkane	Olefins	Alkane
150–153, 156 159–161, 167, 168[b–d]	1,4-Diiodobutane	90 ± 1	8 ± 1 C_2H_4 2 ± 1 1-Butene	
174[e]	1,4-Dibromobutane	97	3 C_2H_4	
203[e]	1,4-Dichlorobutane	100	Tr C_2H_4	
192–193, 200, 201[f,g]	1,5-Diiodopentane	73 ± 2	27 ± 2 1-Pentene	
205, 208, 209, 212, 215, 217	1,5-Dibromopentane	92 ± 2	4 ± 1 1-Pentene	4 ± 2
210, 211	1,5-Dichloropentane	97–98	Tr 1-Pentene	2–3

[a] Figures are yield percentages of the reduction products, *i.e.*, total reduction product yield = 100%. Absolute yields of reduction products are given in Table I. [b] Experiments 150–153 and 156 were done by injection of the iodide into the sodium naphthalene solution. Experiments 159–161 were evaporation experiments (see Experimental Section). Experiments 167–168 were done by injecting small portions of sodium naphthalene into a solution of the alkyl iodide until the green color persisted. No yield variations among these reaction techniques were observed. [c] In experiment 156 the substance giving rise to the vpc peak attributed to cyclobutane was trapped from the vpc. It gave rise to an nmr spectrum (in CCl_4) with a single peak at δ 1.97 ppm, as reported for cyclobutane (cited by J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N J., 1965, p 86). [d] In experiment 167 the substance giving the vpc peak attributed to cyclobutane was led into a Hitachi RMU6 mass spectrometer; the resulting spectrum matched in detail that reported for cyclobutane ("Mass Spectral Data," compiled by the American Petroleum Institute, Research Project 44, Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburg, Pa.). In the same experiment, the vpc analysis was extended to the region of alkylation products. Four peaks were observed, each of which gave a parent ion (m/e 184) corresponding to $C_{14}H_{16}$; total yield, 44%. This m/e is consistent with the alkylation products reported by D. Lipkin, G. J. Divis, and R. W. Jordan, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **13**, D60 (1968), from the reaction of 1,4-dichlorobutane with sodium naphthalene in THF. The products were tetramethylene dihydronaphthalenes and butylnaphthalenes. [e] Cyclobutane was confirmed by vpc–mass spectrometry as described above. [f] Experiments 192 and 194 involved alkyl halide injection into sodium naphthalene solutions. Experiments 193, 200, and 201 were "evaporation" experiments. No product variations with technique were observed. [g] In experiment 201, the yield of materials corresponding to four peaks in the vpc region of alkylation products was 50%. We regard the alkylation product yield as less reliable than that of reduction products.

of sodium naphthalene with α,ω-dihaloalkanes.[26–28] Thus the "same" diradicals cannot be involved in both kinds of reactions (unless there is a substantial difference in reactivity patterns between gas and solution phases). However, diradicals formed in the gas phase reactions of α,ω-dihaloalkanes with alkali metals (at 200–300°)[20–23] could be the "same" as in reactions of sodium naphthalene with 1,4-diiodobutane and 1,5-diiodopentane. For 1,4-dihalobutanes, the mole ratio (2-cyclobutane/ethylene) from gas phase alkali metal reactions varies with temperature;[22] extrapolation to room temperature implies much more cyclobutane than olefin, which correlates with the reaction of 1,4-dihalobutanes with sodium naphthalene in DME. For 1,5-dichloropentane, the ratio cyclopentane/1-pentene is temperature independent at 2.3 for the gas phase alkali metal reactions.[23] This correlates well with the reaction of 1,5-diiodopentane with sodium naphthalene in DME (cyclopentane/1-pentene = 2.8) but not with the similar reactions of 1,5-dibromopentane and 1,5-dichloropentane. Thus, there is a possible kinship between reactions of dihaloalkanes with gaseous alkali metals at 200–300° and reactions of diiodoalkanes with sodium naphthalene in DME, but the kinship does not extend to reactions of dibromo- and dichloroalkanes with sodium naphthalene. Perhaps the reactions of diiodoalkanes follow Scheme V while those of dibromo- and dichloroalkanes do not.

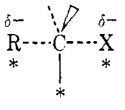
Another alternative is that reaction 2 followed by diradical collapse is significant for the diiodides, but not for the dibromides and dichlorides, and that the diradical product of reaction 2 collapses to a large extent to olefin, while ω-haloalkylsodiums give mostly cycloalkane.[29] This interesting possibility cannot be ruled out rigorously, but in view of the fact that the yield of 1-pentene is 15% but the yield (1-pentene + cyclopentane) is the "normal" ~58%, the arguments made previously against reaction 2 seem to apply in full force.

Yet another alternative is that some of the reduction products are formed through reactions 7, which would

$$XCH_2(CH_2)_{n-2}CH_2Na \xrightarrow{NaC_{10}H_8} \cdot CH_2(CH_2)_2CH_{n-2}Na \longrightarrow \text{cyclo}(CH_2)_n + Na\cdot \quad (7)$$

compete with intramolecular cyclizations of ω-haloalkylsodiums. The fact that no dependence of the product distribution on the concentration of sodium naphthalene was found militates against this possibility.

Finally, perhaps Schemes IV and V do not properly represent alkyl dimer and cycloalkane formation. A remaining alternative is an atypical nucleophilic displacement. Frontside displacements and distorted E2 transition states could result from the requirements of interionic forces in solvents of low dielectric constants ($D \simeq 7$ for DME, THF, and MeTHF). In **2**, an S_N2



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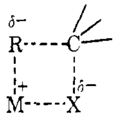

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transition state, the asterisks (*) mark possible locations of an associated metal ion, but none of these place the metal ion in simultaneous proximity to both groups bearing large fractions of the negative charge. On the other hand, **3**, a frontside displacement or four-center transition state, provides for good interionic contact throughout.

Solvent and Metal Ion Effects. We have examined the solvent and metal ion effects on the distribution between reduction and alkylation and on the distribu-

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(26) E. K. C. Lee, *J. Phys. Chem.*, **71**, 2804 (1967).

(27) S. W. Benson and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **64**, 80 (1942).

(28) R. G. Shortridge, Jr., and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 2228 (1970).

(29) We thank S. Bank for this suggestion.

Table IV. Percentages of Reduction Products from Reactions of Dihaloalkanes with Alkali Naphthalenes in Ethers^a

Dihaloalkane	Solvent	Li^+	Na^+	Cs^+
1,4-Diiodobutane^b	DME	59 ± 1 (4)	56 ± 2 (10)^c	42 ± 1 (4)
	THF	54	40	42
1,5-Diiodopentane^d	DME	62	57 ± 2 (5)^e	40
	MeTHF		32^f	
1,5-Dibromopentane^d	DME	61 ± 0 (2)	57 ± 4 (6)	40
	THF		40 ± 0 (2)	

^{a} Values given are yields (%), based on alkyl halide consumed, of combined reduction products. The observed limits of variation are shown with the number of experiments in parentheses. ^{b} Reduction products = cyclobutane and ethylene (trace 1-butene). ^{c} Directly determined yield of alkylation products is 44%, accounting for 100% of the reactant alkyl halide. ^{d} Reduction products = cyclopentane and 1-pentene (small amounts of pentane). ^{e} Directly determined yield of alkylation products is 50%, accounting for 107% of the reactant alkyl halide. ^{f} Directly determined yield of alkylation product is 64%, accounting for 96% of the reactant alkyl halide.

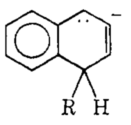
Table V. Solvent and Metal Ion Effects on Reduction Product Ratios (Cycloalkane/Olefin) in Reactions of Dihaloalkanes with Alkali Naphthalenes^a

Dihaloalkane	Solvent	Li^+	Na^+	Cs^+
1,4-Diiodobutane^b	DME	13 ± 1 (4)	12 ± 2 (10)	9.4 ± 0.1 (4)
	THF	13	9	10
1,5-Diiodopentane^c	DME	2.9	2.8 ± 0.2 (5)	4.7
	MeTHF		8	
1,5-Dibromopentane^c	DME	59 ± 0 (2)	22 ± 5 (6)	38
	THF		37 ± 0 (2)	

^{a} Values tabulated are yield ratios of products cycloalkane/olefin. The observed limits of experimental variations are shown with the number of experiments in parentheses. Where no variation is shown, the figure represents one experiment. ^{b} Cycloalkane = cyclobutane; olefin = ethylene. ^{c} Cycloalkane = cyclopentane; olefin = 1-pentene.

tion among reduction products. Data on the reduction–alkylation distribution are found in Table IV. The effects of solvent and metal ion variation, among DME, THF, 2-methyltetrahydrofuran (MeTHF), Li^+, Na^+, and Cs^+, are small but definitely outside experimental error. Further, they follow an interesting pattern. In each case for which independent data suggest that ion pairs of the alkali naphthalene are predominantly solvent separated (Li^+–DME, Li^+–THF, and Na^+–DME),[30,31] the reduction product yield is about 58%. In the other cases, for which the alkali naphthalene ion pairs are believed to be less solvated (contact ion pairs), the reduction product yield is about 40%. There may be a trend to even less reduction in poorer cation solvating media than THF, that is, the 32% reduction found for the reaction of 1,5-diiodopentane with sodium naphthalene in MeTHF may be significantly less than the 40% found for contact ion pairs in DME and THF.

These solvent and metal ion effects are so small, an extreme variation of less than a factor of 3 in the rate constant ratio for reduction and alkylation, that interpretation is probably not justifiable. However, it may be worth pointing out that the direction of the trend is rationalized by the following reasoning. While the combination of an alkyl radical with the naphthalene radical anion leads to a product anion **4** with a structure not very different from the naphthalene radical anion itself, the electron-transfer reduction process leads to a highly localized alkyl anion. In solvents of low dielectric constant, the cations will be "stuck" rather to the anions. For the combination of alkyl and naphthalene anion radicals, the cation can remain essentially in its original position. On the other hand, for the reduction of the alkyl radical, the cation must move from a position of association with the naphthalene radical anion to association with the product alkyl anion. Accompanying solvation reorganization must also occur. It is reasonable to suppose that decreased cation solvation may hinder cation relocation, since the cation would then be more tightly bound to the naphthalene radical anion.[32] This leads to the prediction that less polar ethers should favor radical combination relatively, as is observed.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Turning to the effects of solvent and metal ion on the distribution among reduction products, we find again rather small effects (Table V). However, some of the observed effects are even more definitely outside experimental error. For 1,5-diiodopentane, especially, it appears that less solvated cations (Cs^+) and poorer cation solvating solvents (MeTHF) favor relatively more cyclopentane. This seems to imply that there are definitely aggregation and solvation influences, as well as halogen effects, on the reactions of 5-halopentylalkalies.

Reaction of 2,5-Diiodohexane with Sodium Naphthalene in DME. 2,5-Diiodohexane provides a secondary radical which then reacts with sodium naphthalene according to Scheme III. Sargent and Lux have reported that secondary and tertiary alkyl iodides give less reduction and more alkylation than primary

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(30) N. Hirota, R. Carraway, and W. Schook, *J. Amer. Chem. Soc.*, **90**, 3611 (1968).

(31) Y. Karasawa, G. Levin, and M. Szwarc, *J. Amer. Chem. Soc.*, **93**, 4614 (1971).

(32) It is reasonable to suppose that initial stages of separation of ions of contact ion pairs should require more energy than a similar process for solvent separated ion pairs. However, it should be kept in mind that in solvents for which solvent separated ion pairs are favored, separation of contact ion pairs to solvent separated ion pairs involves a *decrease* in free energy.

alkyl iodides.[12] However, with simple iodides, the quantification of this effect is somewhat uncertain, since there are reactions subsequent to reduction leading to dimers, olefins, and additional alkane. The diiodoalkanes provide a cleaner system.

We examined the reaction of 2,5-diiodohexane briefly, determining the combined yield of C_6 hydrocarbons. This was 46%, confirming the findings of Sargent and Lux. Thus, it appears that the reduction alkylation ratio is 1.4 for primary radicals and 0.85 for secondary radicals. This is a small effect, but it is consistent with the traditional order of carbanion stabilities in solution $1° > 2° > 3°$. Since reduction leads to a carbanion, it appears that the thermodynamics of carbanion formation may be reflected in the rate of the reduction process.

The observed trend in reduction/alkylation is certainly not consistent with alkylation *via* an initial SN2 reaction step, as was pointed out by Sargent and Lux.[12] Other data also rule out an initial SN2 step.[33]

Reactions of Alkyl Halides with Sodium Anthracene. From sodium anthracene in DME, reduction products were obtained in very low yields. 5-Hexenyl chloride gave only about 1% 1-hexene and methylcyclopentane combined. 1,4-Diiodobutane gave 1.5% cyclobutane and ethylene. It is clear that reduction is not the major pathway. The indications are, however, that the mechanism of Scheme I applies. This would account for the formation of *some* reduction products and for the detection of methylcyclopentane, which would result from the cyclization of intermediate 5-hexenyl radicals, from 5-hexenyl chloride.[5]

It appears that the reactions of sodium anthracene with primary alkyl radicals are mostly combination, with very little electron-transfer reduction of the alkyl radical. It should be noted that reduction of the alkyl radical is thermodynamically less favored for anthracene than for naphthalene radical anion, since anthracene is much more readily reduced than naphthalene.

It might be expected that a radical with a higher electron affinity, one with an electron-withdrawing group near the radical site, might be reduced to a greater extent than a simple primary alkyl radical. Thus, we examined the reaction of tetrahydrofurfuryl bromide with sodium anthracene. Here the expected reduction product is 4-penten-1-ol, formed by the ring opening of tetrahydrofurfurylsodium. In two experiments, 4-penten-1-ol resulted in 53 ± 7% yield. In reactions with sodium naphthalene in DME, the yield of 4-penten-1-ol is 83 ± 5% for tetrahydrofurfuryl iodide, bromide, and chloride. The reaction of sodium naphthalene in THF with tetrahydrofurfuryl chloride gives 65% 4-penten-1-ol.

Qualitatively, all these experiments parallel trends observed in other systems. For a given sodium arene, tetrahydrofurfuryl radicals give more reduction than simple primary alkyl radicals. For a given alkyl halide, including tetrahydrofurfuryl halides, sodium naphthalene gives more reduction than sodium anthracene. For the reaction of a given alkyl halide, including tetrahydrofurfuryl halides, with sodium naphthalene, DME as the solvent gives more reduction than THF.

Relationship to Electrochemical Reductions. Electrochemical reductions of alkyl halides are believed to follow mechanisms parallel with Scheme I (reduction branch only), involving initial radical formation then reduction to a carbanion which reacts with the solvent, supporting electrolyte, or other species present.[34] Rifi has examined the electrolyses of 1,3-dibromopropane, 1,4-dibromobutane, and 1,5-dibromopentane in DMF (n-Bu_4NClO_4) at 40–50 V and 0.3–0.5 A.[37] Cyclopropane was formed exclusively from 1,3-dibromopropane, but 1,4-dibromobutane gave cyclobutane/n-butane = 1:3, while 1,5-dibromopentane gave only n-pentane. Rifi concluded that products could arise through internal displacements of ω-haloalkyl anions or, possibly, through analogous concerted processes occurring at the electrode. Except for the intrusion of the saturated linear alkanes, the electrochemical results resemble those obtained here by reduction in homogeneous media.

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

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(34) Reviews are given in two recent monographs.[35,36]

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(37) M. R. Rifi, *J. Amer. Chem. Soc*,, **89**, 4442 (1967).