in rate which occurs in the same interval. These data do not enable us to determine whether changes in solvation are also important, although changes in transition-state solvation could possibly be of a magnitude to produce the observed change in isotope effect.

Relation to Studies of Enzymes. The decarboxylation of 4-pyridylacetic acid is a good model reaction for the decarboxylation step of pyridoxal 5′-phosphate dependent decarboxylases and other decarboxylations involving zwitterionic starting states. We have suggested[1] that decarboxylases work by providing a nonpolar active site for decarboxylation. Our analysis of isotope effects on enzymatic decarboxylations has always been predicated on the assumption that the intrinsic carbon isotope effect on the decarboxylation step in such a nonpolar environment would be about the same as that observed in aqueous solution. This study provides confirmation of that assumption.

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Registry No. 4-Pyridylacetic acid, 28356-58-3; carbon-13, 14762-74-4.

Product Ratio Variation in Reactions of *o*-(3-Butenyl)halobenzenes and 6-Bromo-1-hexene with Alkali Metals in Ammonia/*tert*-Butyl Alcohol Solution. Indications of Reaction-during-Mixing Effects

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Abstract: The four *o*-(3-butenyl)halobenzenes, on reaction with K, Na, or Li in 67% ammonia/33% *tert*-butyl alcohol medium, afford mainly 1-methylindan, considerable 3-butenylbenzene, and some 1,2-bis(1-indanyl)ethane. The first and third of these products are believed to result from cyclization of intermediate *o*-(3-butenyl)phenyl radical. The variation of product ratio with the identity of the halogen is inconsistent with a conventional assumption of reaction with the solvated electron in homogeneous solution and seems better accounted for by a model of reaction in local surroundings of steep concentration gradients during mixing of species through diffusion. 6-Bromo-1-hexene affords very little methylcyclopentane during reaction with potassium in this medium.

The four familiar halobenzenes behave quite differently in their $S_{RN}1$ reactions with acetone enolate ion in ammonia, provoked by dissolved potassium metal.[1] All four give the same three principal products, phenylacetone, 1-phenyl-2-propanol, and benzene, but the ketone/alcohol ratio decreases sharply as the halogen changes from iodine to fluorine, and the percent of benzene increases steeply as the same change of halogen occurs. It has been suggested[1] that these trends are consequences of the occurrence of reaction during mixing; in that case, strong concentration gradients exist and relatively small changes in the timing of chemical events can affect the environment in which ensuing intermediates must react, and therefore the stable products eventually formed.

We desired to explore some further system in which aryl halides would react with solvated electrons to form aryl radicals, via $ArX^{\bullet-}$ intermediates, and in which the aryl radicals would be able to partition between different modes of reaction. For this purpose we chose to study the action of alkali metals on the four *o*-(3-butenyl)halobenzenes; the solvent chosen was 67% ammonia/33% *tert*-butyl alcohol.[2] Work by Beckwith and associates[5,6] has demonstrated that the *o*-(3-butenyl)phenyl radical cyclizes readily to the 1-indanylmethyl radical. The alterntive mode of reaction of the aryl radical would be to accept a further electron to form the aryl anion which on being hydronated[7] would afford 3-butenylbenzene.

Results

Reactions of 6-Bromo-1-hexene (1). Actually we first investigated an allied system, namely, one involving the thoroughly investigated[8,9] 5-hexenyl radical cyclization. The anticipated events, upon reaction of 6-bromo-1-hexene with solvated electrons

Scheme I

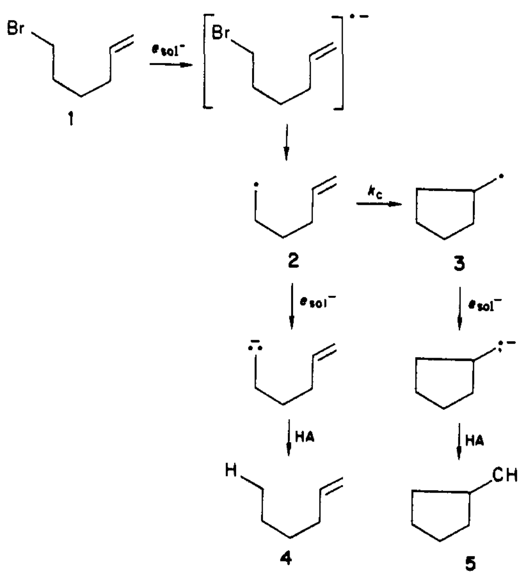

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Table I. Treatment of 6-Bromo-1-hexene (**1**) with Potassium in 67% Ammonia/33% *tert*-Butyl Alcohol at Reflux[a]

						cyclization half-lives[d]	
1, mmol	K, mmol	**4**, %	**5**, %	dimer,[b] %	**1**,[c] %	est. A	est. B
10	22	68.9	0.63	*e*	nil	0.013	
10	22	63.6	0.70	20.7	nil	0.016	0.012
10	22	63.5	0.66	18.7	nil	0.015	0.012
10	22	56.2	0.47	18.9	4.8	0.012	0.009
3.33	7.3	50.7	0.62	15.0	24.4	0.018	
10	26[f]	61.4	2.07	16.6	nil	0.048	0.038

[a] Solvent volume 100 mL unless otherwise noted. [b] 1,11-Dodecadiene. [c] Recovered **1**. [d] For estimate A, $[\mathbf{2}]_0 = a([\mathbf{4}]_t + [\mathbf{5}]_t)$ and $[\mathbf{2}]_t = a[\mathbf{4}]_t$, where *a* is a proportionality constant, and subscripts 0 and t designate initial and final concentrations; for estimate B, $[\mathbf{2}]_0 = a([\mathbf{4}]_t + [\mathbf{5}]_t + 2[\text{dimer}]_t)$ and $[2]_t = a([\mathbf{4}]_t + 2[\text{dimer}]_t)$. [e] Not determined. [f] Solvent volume 900 mL.

Table II. Products from Treatment of *o*-(3-Butenyl)halobenzenes (6) with Potassium in 67% Ammonia/33% *tert*-Butyl Alcohol under Standard Conditions[a]

substrate	n[b]	**10**, %	**11**, %	dimer,[c] %	substrate,[d] %	**11**/**10**[e]	cyclizn $t_{1/2}$'s[f]
6f	2	34.7 ± 2.0	53.1 ± 1.3	nil	11.2 ± 1.0	1.5 ± 0.1	1.3
6c	2	17.6 ± 0.4	78.2 ± 2.5	ca. 3	nil	4.44 ± 0.05	2.5
6b	4	9.6 ± 0.2	72.1 ± 2.3	18.4[g]	nil	7.5 ± 0.4	3.4
6i	5	7.5 ± 0.8	57.7 ± 5.1	17.1 ± 0.1	17.6 ± 4.9	7.7 ± 0.4	3.5

[a] Conditions: at reflux in solvent of *tert*-butyl alcohol (33 mL) with NH_3 added to total 100 mL, with 0.01 mol of 6 and 0.022 mol of K being used. The standard deviations of yield among replicate experiments are shown. [b] Number of experiments reported. [c] 1,2-Bis(1-indanyl)ethane (all stereoisomers). [d] Recovered 6. [e] Reckoned from average yields in this table. [f] See Discussion. [g] Determined in one experiment only.

Table III. Products from Treatment of *o*-(3-Butenyl)chlorobenzene (**6c**) with Potassium under Various Conditions[a]

6c, mmol	K, mmol	*t*-BuOH	NH_3, mL	**10**, %	**11**, %	**6c**, %	**11**/**10**	conditions
10	22	33 mL	67	17.9	80.0	nil	4.5	
10	22	33 mL	67	17.5	76.5	nil	4.4	
10	22	2.2 mmol	100	17.8	68.5	nil	3.8	
10	22	2.2 mmol[b]	100[b]	18.7	76.2	nil	4.1	Me_3CNH_2 cosolvent[b]
10	13	33 mL	67	13.1	46.5	35.0	3.5	
10	6.5	33 mL	67	8.9	26.5	61.9	3.0	
10	3.0	33 mL	67	4.0	11.5	78.5	2.8	
6.7	13	33 mL	67	11.5	74.0	14.5	6.4	
3.3	6.5	33 mL	67	7.2	82.7	12.8	11.5	
2.0	4.4	33 mL	67	4.6	93.6	nil	20.1	
2.0	4.4	4.8 mmol	100	7.9	93.5	nil	11.8	(appeared dissolved)
10	22	25 mmol	100	11.5	57.2	27.2	5.0	inverse addition[c]
10	22	33 mL	67	17.8	78.0	2.4	4.4	20 bits of K
10	22	33 mL	67	17.2	75.8	d	4.4	2 chunks of K
10	22	33 mL	67	16.4	78.9	nil	4.8	no stirring
10	22	33 mL	67	24.8	72.5	nil	2.9	26 000 rpm stirring
10	22	33 mL	67	24.8	68.5	nil	2.8	26 000 rpm stirring
10	22	33 mL	67–117[e]	15.4	81.9	nil	5.3	K in NH_3 added with rapid stirring[e]
10	22	33 mL	67	12.6	77.3	4.3	6.1	K in NH_3 added with normal stirring[f]

[a] Unless otherwise noted, about 10 lumps of K added to 6c in the stated solvent, with gentle stirring. [b] *tert*-Butylamine (33 mL) was solvent component. [c] The 6c and *tert*-butyl alcohol were added to K in NH_3. [d] Not determined. [e] The K dissolved in 50 mL of NH_3 was added to solution of 6c in 33 mL of *tert*-butyl alcohol and 67 mL of NH_3, with 26 000 rpm stirring. [f] As in *e*, except 1000 rpm stirring.

(from potassium metal), are shown in Scheme I. Results are presented in Table I.

It is noteworthy that little cyclization to methylcyclopentane (**5**) occurred. The main product was 1-hexene, and the second in prominence was a dimer identified as 1,11-dodecadiene.

In the last two experiments of Table I, the concentration of **1** was lower than in the rest. In the next-to-last, the amount of **1** present in the usual 100 mL of solvent was reduced by a factor of 3, while in the last the solvent volume was increased 9-fold. In the last experiment it is noteworthy that relatively more cyclization occurs when the substrate concentration is lower.

According to the model of Scheme I, the 5-hexenyl radical (**2**) may either cyclize or be electronated to form the 5-hexenyl anion. How much cyclization can occur should depend on how long radical **2** exists before it is electronated. One can estimate from the data of Table I the average number of cyclization half-lives that were available.[10] Two such estimates, on slightly different bases, are given in the last two columns of Table I.

Reactions of *o*-(3-Butenyl)halobenzenes (6). These were expected to occur according to the mechanisms outlined in Scheme

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(2) We have been unable to find data concerning the lifetime of the solvated electron in *t*-BuOH, much less in 67% ammonia/33% *t*-BuOH. The half-lives of the solvated electron in other alcohols, underestimated because the observations were perturbed by a contribution from reaction with the radical cation of the solvent, range from 1.5×10^{-6} s in methanol to 5×10^{-6} s in 2-propanol.[3] The half-life in *t*-BuOH is probably longer, and in 67% ammonia/33% *t*-BuOH still longer, and at −28 °C longer yet; a half-life in excess of 1×10^{-5} s is probable. The reaction of potassium with *t*-BuOH in ammonia[4] is slow enough to be inconvenient in preparative work.

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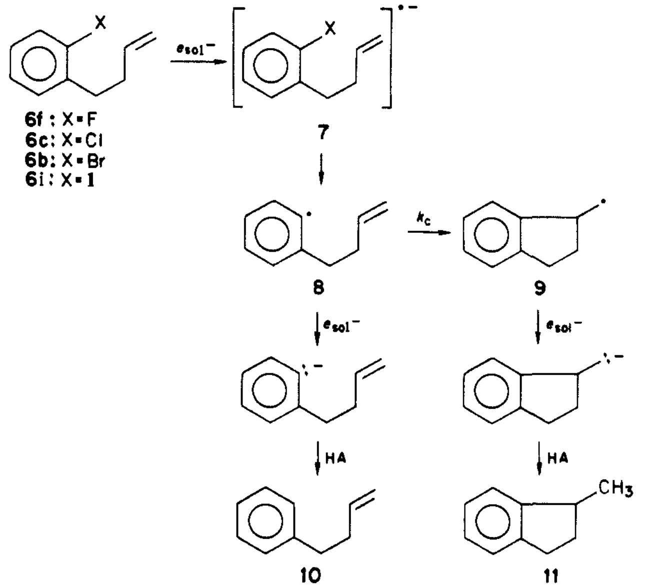
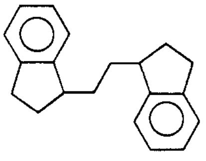
(10) The numbers of half-lives were reckoned from the familiar first-order equations: $\ln([A]_0/[A]_t) = kt$ and $\ln 2 = kt_{1/2}$. Division of the former by the latter gives $t/t_{1/2} = \ln([A]_0/[A]_t)/\ln 2$. When one takes the yield of dimer into account in reckoning the number of half-lives that have transpired, as in estimate B, Table I, one does not double the percent yield of dimer because the percent yield of dimer is calculated as 200 (mol of dimer)/(mol of RX).

Scheme II



II. The four substrates of structure **6** were treated with potassium metal under standard conditions. Results are summarized in Table II. Besides the cyclized (**11**) and uncyclized (**10**) dehalogenation products, significant amounts of a dimer identified as 1,2-bis(1-indanyl)ethane (**12**) were obtained in some experiments.



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Two trends are evident in Table II. The ratio of **11** to **10** increases strongly as the atomic number of the halogen increases, from 1.5 with **6f** to 7.7 with **6i**. Also, the yield of dimer **12** is sharply dependent on the identity of the halogen; no **12** was detectable as a product from **6f** whereas about 18% of **12** was formed from **6b** and **6i**.

In reckoning the number of cyclization half-lives as listed in Table II,[10] we took $[8]_0$ to be the sum of the concentrations of **10** and **11** and twice the concentration of **12** formed and $[8]_t$ to be the concentration of **10** formed.

Inasmuch as **12** has two similar chiral centers, it is expected to be able to exist as three stereoisomers, a racemic pair and a meso form. We observed the formation of approximately equal amounts of isomeric substances which we take to be the racemic and meso forms, one of which crystallized, but we are unable to say which is which.

Several experiments summarized in Table III were conducted with **6c** in order to determine the effects of various reaction conditions on the ratio of **11** to **10**. In general, the **11**/**10** ratio was little affected by alteration of the conditions; mostly it ranged between 2.8 and 4.8. It mattered little whether the solvent was ammonia containing a small amount of *tert*-butyl alcohol (*t*-BuOH) to neutralize the KNH_2 otherwise formed, or whether it was 67% ammonia/33% *t*-BuOH, or whether it was ammonia/*tert*-butylamine. Also of little consequence were the order of addition of reactants, the rate of stirring, or the condition of the potassium introduced. The results were much the same from an unstirred reaction and from one stirred by a high velocity stirrer. Potassium introduced as a solution in ammonia as small bits or as large chunks brought about much the same result.

The one experimental factor that does consistently affect the **11**/**10** product ratio is substrate concentration. At the usual initial substrate concentration of 0.1 M, the **11**/**10** ratio is about 4, but it increases as the substrate becomes more dilute. In one experiment with **6c** initially 0.02 M, the **11**/**10** ratio was 20.

Table IV. Products from Treatment of **6f** and **6c** with Various Alkali Metals in 67% Ammonia/33% *tert*-Butyl Alcohol[a]

substrate	metal	metal, mmol	**10**, %	**11**, %	**6f**,[b] %	**11**/**10**
6f	Li	20	39.4	53.3	7.2	1.4
	Na	20	35.2	62.3	4.6	1.8
	K[c]	22	36.1	52.2	10.6	1.4[c]
	K[c]	22	33.3	54.0	11.9	1.6[c]
6c	Li	20	13.7	71.9		5.2
	Li	22	10.4	57.0		5.5
	Na	6.5	6.9	21.6	*d*	3.1
	Na	20	14.3	75.4		5.3
	Na	22	7.9	64.5		8.2
	K	22	17.7	78.3		4.4

[a] All experiments involved 10 mmol of **6f** or **6c** in 100 mL of solvent. [b] Recovered substrate. [c] Averaged results from the two experiments with **6f** and K appear in Table II. [d] An unquantified amount of **6c** was recovered.

The effect of changing the alkali metal was investigated, as displayed in Table IV. Briefly, with either **6f** or **6c**, changing the metal from K to Na or Li makes little difference. The small differences in **11**/**10** ratio tabulated appear to be randomly related to the identity of the metal; indeed, the differences in product ratio between three experiments with **6c** and Na are greater than those between experiments with different metals.

Discussion

We take the mechanisms of the dehalogenation reactions that we have studied to be as represented in Schemes I and II. These mechanisms are similar to those assigned on good evidence[11] to reactions of alkyl halides with sodium naphthalenide and like reagents.

Cyclization Products Not Carbanion Derived. We now ask whether the 5-hexenyl and *o*-(3-butenyl)phenyl carbanions of Schemes I and II, respectively, are able to cyclize significantly under the conditions of our experiments. Koppang, Ross, Woolsey, and Bartak[12] have shown that the *o*-(3-butenyl)phenyl anion can cyclize to form 1-indanylmethyl anion in substantial amount. They observed, however, that cyclization was strongly suppressed by 0.4 M deuterium oxide in their dimethylformamide solvent. Inasmuch as our solvent was about 3.5 M in *t*-BuOH and *t*-BuOH hydronates benzyl carbanion nearly as rapidly as water does,[13] we judge that the anion cyclization route to **11** was significant in our experiments.

There is reason to believe that the 5-hexenyl anion would cyclize to cyclopentylmethyl anion, if it were not in the presence of a good hydron donor. 5-Hexenyllithium, in pentane/diethyl ether solution at 20 °C, cyclizes to cyclopentylmethyllithium with the rate constant 2.06×10^{-3} s^{-1} ($t_{1/2}$ 336 s).[14] In ether solvents, 1-methyl-5-hexenylsodium cyclizes to (2-methylcyclopentyl)methylsodium at an undefined rate.[15]

We have no certain information as to the rate of hydronation of the 5-hexenyl anion under our conditions. A useful guide, however, is the measurement by Bockrath and Dorfman[13] of the rate constants for hydron transfer to benzyl anion from water and four alcohols in tetrahydrofuran solution. For benzyl anion paired with Na^+, the rate constants are 1.3×10^9 M^{-1} s^{-1} with *t*-BuOH and 5.5×10^9 M^{-1} s^{-1} with water.[16] Assuming that reactions so fast have negligible temperature coefficients, and that the solvent effect of ammonia is the same as of tetrahydrofuran, we estimate the first-order rate constant for hydronation of the benzyl an-

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(16) For free benzyl anion, the rate constants are a little lower.

ion/sodium ion pair in our system as 4.6×10^9 s^{-1}, for a half-life of 1.5×10^{-10} s. Inasmuch as the 5-hexenyl anion is surely more basic than benzyl anion, these estimates should if anything overstate the lifetime of the 5-hexenyl anion in our experiments.

We expect the rate of cyclization of 5-hexenyl anion to exceed that of 5-hexenyllithium, but we doubt that it exceeds it by the 12 powers of ten that would be necessary to make its cyclization rate competitive with its destruction by hydronation. We judge cyclization of this anion in our experiments to be negligible.

Electronation of Radical Intermediates. An important feature of the systems investigated, as we understand them, is the very high velocity of electronation of radicals **2**, **3**, **8**, and **9** by solvated electrons. Because the electronation of radicals is exoenergetic,[17] reactions of radicals with the solvated electron probably occur at or above encounter-controlled rate,[22] a rate that is very high because of the high mobility of the solvated electron.[23] A rate constant exceeding that for encounter is conceivable because electron migration may occur in part by tunneling.[24] Provisionally, we suggest a rate constant on the order of 10^{11} M^{-1} s^{-1} for electronation of the radicals involved in our systems.[25] We note that other workers[28] have judged reactions whereby aryl radicals are electronated by radical anions of aromatic compounds or by cathodes to occur at encounter-controlled rate. Also, there is evidence that alkyl radicals are rapidly electronated by the naphthalene radical anion in solvents such as tetrahydrofuran.[11]

The Environment of Reaction. Solution reactions familiarly occur in homogeneous medium, on a time scale of seconds or longer. That is, however, not the case for the reactions we report. We know because the blue color characteristic of solvated electrons never spreads throughout the flask to form a uniformly blue solution. When reaction is conducted by adding bits of alkali metal to a stirred solution of **1** or **6**, we usually do see little streaks of blue trailing behind the bits of metal as they float about, but no more blue than that. The locus of reaction must therefore be at or near the bits of metal. Reaction does not, however, occur uniquely at the metal surface, for we obtained essentially the same results when the metal was provided as a solution in ammonia as when bits of metal were added. That uniform, homogeneous solutions are not obtained is understandable in terms of the very high reactivity of alkyl and aryl halides with solvated electrons (see below).

Possibilities remaining are that reaction occurs in a locally homogeneous situation in the blue streak near a bit of metal or that it occurs in circumstances of strong concentration gradients. If the medium were one of uniform solvated electron and substrate concentrations, the four *o*-(3-butenyl)halobenzenes (**6**) should not give significantly different product proportions, for radical **8** would be formed in essentially the same surroundings regardless of the halogen originally present. (The solvated electron concentration would drop as reaction occurred, but at any fraction of reaction it ought to be the same, say, for **6i** as for **6c**, and therefore both substrates should give products in the same ratio.)

The variation of product proportions as the concentration of **6c** is varied (Table III) constitutes further evidence that the reaction environment is not homogeneous even in a local sense. The product ratio **11**/**10** *increases* as the concentration of **6c** *decreases*. Were the reaction occurring in a nearly homogeneous local volume element near the dissolving metal, at high concentrations of **6c** we would expect a relatively large number of solvated electrons to be consumed in the initial electronation. That would leave a relatively lower concentration of electrons surviving as such. Radical **8** should then have experienced less competition from electronation to *o*-(3-butenyl)phenyl anion and have undergone relatively more cyclization to radical **9** (see Scheme II), leading to a higher **11**/**10** ratio at higher substrate concentration, the opposite of what we observed.

We therefore judge that reaction occurred during mixing, in local conditions of strong concentration gradients.

Initiation with a Termination Reagent. In Scheme I or II, the electron that initially reacts with **1** or **6** performs an initiation function, in the terminology of radical chain reactions, whereas the electrons that react with **2**, **3**, **8** or **9** effect termination. We have, in effect, studied radical reactions initiated with a good termination reagent. From that point of view, it is remarkable that we obtain any cyclization products at all.

The Time Interval Hypothesis. For the reactions of phenyl halides with acetone enolate ion, provoked by alkali metals, that were mentioned in the introduction, it has been proposed that there is a time interval between the arrival of initiating and terminating electrons at some microscopic volume element in which a particular halobenzene exists and reacts.[1] It was suggested that product proportions were determined by the extent to which a radical chain mechanism could operate during that time interval before terminating electrons arrive.

Termination, as a second-order reaction, must have a half-life dependent on the concentration of solvated electrons present. If we correctly surmise that the rate constant for termination is about 10^{11} M^{-1} s^{-1}, the half-life would be about 0.1 ns if the electrons were 0.1 M, 1 ns if they were 0.01 M, and so forth. Because the local electron concentration would vary in a system with steep concentration gradients, the time required for termination would be variable.

We show in Table II the number of cyclization half-lives that were available to radical **9**, as derived from the four *o*-(3-butenyl)halobenzenes **6**, under uniform protocol for reaction with potassium metal. That less time is required for the iodo substrate to experience electronation and fragmentation, which transform **6** into **8**, than for the fluoro substrate (to consider the extremes) is expected. Rate constants for reactions of the hydrated electron with the four halobenzenes[30] and for the fragmentation of aryl halide radical anions (to aryl radicals and halide ions)[31,32] both diminish in the order I > Br > Cl > F.

Recent work has made it possible to estimate the rate constant (k_c in Scheme II) for cyclization of **8** to **9**;[29] it is 1×10^8 s^{-1} at our experimental temperature of -28 °C, for a half-life of 6.9×10^{-9} s. Using this value and the data in Table II, we reckon the time available for cyclization of **8** to be 24 ns for **6i** and **6b**, 17 ns for **6c**, and 9 ns for **6f**. These estimates must be regarded as averages. The distribution of lifetimes that is averaged in any example is, however, unclear.

If conditions were such as to provide a more or less uniform time interval between the arrival of the initiating and the terminating electrons, why should the time available for radical cyclization differ according to the halogen originally present? The difference arises, according to this hypothesis, from the differing

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(17) The redox potential of the solvated electron in ammonia is large and negative, -2.7 V vs. Ag/AgNO$_3$,[18] whereas the potential of the CH_3^-/$CH_3\cdot$ couple is more positive, -0.45 V vs. Ag/AgCl in water.[19] The electron affinities of the methyl and phenyl radicals in the gas phase are positive (0.08 eV[20] and ca. 1.4 eV[21]) and are likely to be greater in solution where the anion is solvated.

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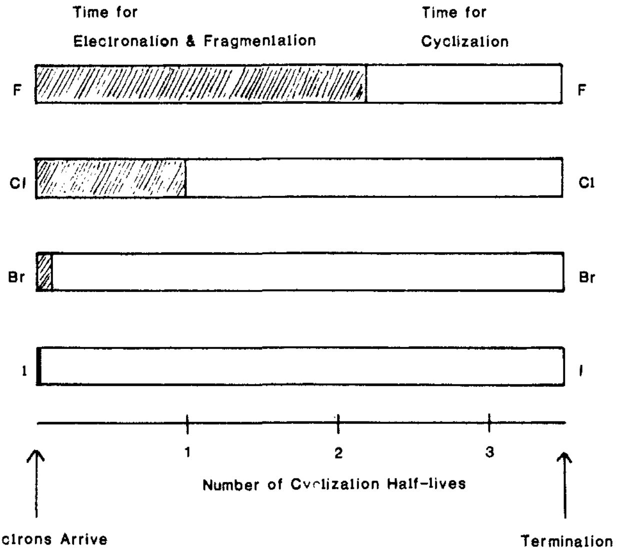

Figure 1. Graphical representation of the time required, after arrival of initiating electrons, for electronation and fragmentation and of the time available for cyclization before terminating electrons arrive.

times required for substrate electronation and for fragmentation of the substrate radical anions.

Because both the electronation of aryl iodides and the fragmentation of their radical anions are exceptionally fast,[30-32] we judge that on a time scale of tens of nanoseconds the time required for electronation and fragmentation of **6i** is negligible. We can therefore take the time available for cyclization of **6b** and **6i**, ca. 24 ns, as an estimate of the average time interval between the arrival of the electron that initiates reaction and the arrival of a second electron that electronates **8** or **9**. We then estimate the time taken for electronation and fragmentation to be 7 ns in the case of **6c** and 15 ns for **6f**.

Our experimental procedures, whether the alkali metal was added as such or in ammonia solution, provided at some early stage a zone of solution rich in solvated electrons in contact with another zone of solution, in the same or nearly the same solvent, containing halogenated substrate but no free electrons. As mixing and diffusion of species occurred, these highly reactive species began to react, and each type of solution penetrated into the zone of the other type. Inasmuch as solvated electrons are especially mobile in ammonia,[23] penetration of the substrate zone by solvated electrons was surely the dominant mode of diffusive mixing. The advancing electrons were in part consumed by reaction with the substrate, so that the leading edge of the electron advance represented a very low electron concentration.

The time interval hypothesis is that the substrate radical anions formed by reaction of leading edge electrons with substrate molecules are generated in an environment nearly electron-free, in which they have an opportunity to react (according to Scheme I or II) until the arrival of more electrons terminates all radical activity. There is a time interval between the arrival of the initiating and terminating electrons. How much cyclization of **2** or **8** can occur during that interval depends on how rapidly substrate electronation and the ensuing fragmentation occur. That time interval begins at different times for different substrate molecules depending on how far they are from the initial electron-rich zone, but for a particular highly reactive substrate the lengths of the time intervals would plausibly cluster about a characteristic value.

A crude graphic representation of the time interval hypothesis is offered in Figure 1. One should bear in mind that the time at the left side of the graph, when electrons arrive, is not the same time for all substrate molecules.

Any extra time available to **8** for cyclization should also be available in part to cyclized radicals **9** for dimerization. The time interval hypothesis would thus lead one to expect that higher **11**/**10** ratios should correlate with higher yields of dimer **12**. Such a correlation is evident in Table II.

From kinetic data for the cyclization of the 5-hexenyl radical,[33] one reckons the half-life at -28 °C to be 35000 ns. If the time interval between the arrival of initiating and terminating electrons were 24 ns, the fully formed radical **2** would be able to cyclize only to the extent of about 0.03%. Our inability to obtain much **5** from reaction of **1** with potassium metal (Table I) is thus qualitatively consistent with the time interval hypothesis.

Why does the **11**/**10** ratio from **6c** increase as the substrate becomes more dilute? (See Table III.) We suggest that the gradient of solvated electron concentration as a function of distance from the main solvated electron solution zone is less steep when the substrate concentration is low then when it is high. In consequence, a low concentration substrate molecule electronated near the electron leading edge will experience the company of only low concentrations of electrons for quite a while, and therefore it will have an increased probability of forming **11**.

Other Hypotheses. We should consider dispassionately all conceivable models, even absurd ones,[34] that might represent our reaction systems and furnish insight into the observed variations of product proportions. We have given considerable attention above to the conventional model of reaction in homogeneous solution and have found it inadequate in several respects. We have discussed among ourselves the possibility that fragmentation of the radical anions of species **6** might give electronically different aryl radicals, depending on the identity of the halogen, that would have different cyclization rate constants, but we find no evidence in the literature for the occurrence of ground-state phenyl radicals differing in electronic conditions. Furthermore, that hypothesis would not illuminate the variation in the **11**/**10** ratio with the concentration of **6c** (Table III).

In conversations, other chemists have suggested that some substrates may require *two* electrons to effect fragmentation. That hypothesis would seem most relevant to the case of **6f**, for aryl fluoride radical anions are comparatively slow to fragment.[35] That hypothesis, coupled with assumption of reaction in homogeneous solution, would not of itself be acceptable; the reaction of the ammonia-solvated electron with fluorobenzene is first order in electrons;[35] also, it would run afoul of difficulties with homogeneous solution models discussed above. On the other hand a small component of cleavage effected by two electrons, especially for **6f**, so as to produce directly a carbanion incapable of cyclization under our conditions, would be compatible with our data and the time interval hypothesis.

In an earlier publication,[1] it was suggested that the product proportion effects mentioned in our introductory paragraph might arise from a mechanical effect during mixing: a small portion of a solvated electron-containing solution might swirl into the solvated electron-free zone, allowing substrate radical anions to be generated away from the main electron-rich zone where they could react for a short while undisturbed by other electrons. If the observed variation of product proportions were of that origin, product proportions ought to have been affected by the conditions of mixing, especially the rate of stirring. In our experience they were not (Table III). Accordingly this model is rejected.

An hypothesis difficult to evaluate at the present time is that substrates **6f** through **6i** may aggregate in part to form microblobs of oily stuff in the 67% ammonia/33% *tert*-butyl alcohol solvent. If the degree of aggregation were dependent on the halogen present, and if substrate molecules present in the microblobs reacted to form **10** and **11** in different ratio than for molecules in true solution, the variation of **11**/**10** ratio with identity of halogen might find explanation. So also might the variation of product ratio from **6c** depending on substrate concentration, there being a larger fraction of substrate truly dissolved at lower total **6c** concentration. Any propensity to aggregate as microblobs should be greater for substrates marginally soluble. Although substrates **6f** through **6i** are marginally soluble in 100% ammonia, they appeared to dissolve readily in our solvent containing 33% *tert*-butyl alcohol. We regard this hypothesis as a conjecture.

Now an adventuresome hypothesis: that substrates **6** are initially electronated in the exocyclic double bond, forming an alkene radical anion,[36] which then effects S_NAr replacement of the halogen. This one is improbable (i) because electronation of such an exocyclic double bond is disfavored[36] and (ii) because **6f** should be the *most* reactive in the

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cyclization step[37] and give the largest proportion of **11**.

Conceivably differential tunneling effects play some role in these systems, affecting either the locus of electronation of **6** (with respect to the boundary between electron-rich and electron-free zones) as a function of the halogen present or the relative access of solvated electrons to the substrate as compared to the radical intermediates. Electrons can tunnel farther to reach aryl iodides than aryl chlorides;[38] this factor could contribute to the greater extent of formtion of **11** from **6i** than from **6c**. However, we have no knowledge of how far electrons may tunnel to reach, say, **8** or **9** as compared to **6b**. We find it difficult to assess the extent to which electron tunneling may affect the observed phenomena.

Concluding Remarks. The striking variation in the **11**/**10** ratio upon treatment of the *o*-(3-butenyl)halobenzenes (**6**) with alkali metals in ammonia/*t*-BuOH medium (Tables II and III) is incompatible with mechanistic models that assume reaction in homogeneous solution. Qualitatively, the product ratios can be rationalized in terms of a model of reaction during mixing at the level of diffusion of chemical species. Objectives for future research will be to test that model further and if possible to demonstrate its inadequacy.[34]

Experimental Section

General. Melting points were determined on a Thomas Hoover Unimelt apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer/10B spectrometer. ^{13}C NMR spectra were measured on a Jeol JNM-FX100S spectrometer operating at 25.125 MHz. ^{1}H NMR spectra were recorded on a Varian EM-360L instrument operating at 60 MHz. All chemical shifts are reported relative to tetramethylsilane. GC-MS were recorded on a Finnigan Model 4000 Automated Gas Chromatograph Mass Spectral System operating, unless stated otherwise, at 70 eV. High-pressure liquid chromatography was carried out on a Waters Associates chromatograph. MS for exact mass were determined at the University of Adelaide, Australia, with use of an AEI MS-3074 instrument. Gas-liquid chromatography (GLC) was conducted on a Hewlett Packard Model 5840A chromatograph equipped with a capillary inlet system. The columns used were the following: column A, 10 m × 0.23 mm vitreous silica WCOT OV-101 silicone fluid; column B, 35 m × 0.23 mm vitreous silica WCOT OV-101 silicone fluid. Commercial samples of 1-hexene and methylcyclopentane were redistilled before use; their purity was shown to be greater than 99% by GLC (column A). 6-Bromo-1-hexene (**1**),[39] 1,11-dodecadiene,[40] *o*-(3-butenyl)chlorobenzene (**6c**),[41,42] *o*-(3-butenyl)iodobenzene (**6i**),[7] and (3-butenyl)benzene[43] were prepared by established methods.

***o*-(3-Butenyl)fluorobenzene (6f).**[42] A solution of *o*-fluorobenzyl chloride (18 g) in anhydrous diethyl ether (50 mL) was added dropwise under nitrogen with stirring to magnesium turnings (3.7 g) (which had previously been activated with a crystal of iodine) in diethyl ether (50 mL). The mixture was boiled under reflux for 60 min. The mixture was cooled, allyl bromide (18 g) was added dropwise, and the mixture was heated at reflux for 20 h. Aqueous 10% HCl (50 mL) was added dropwise to the cooled mixture. The organic phase was separated and washed with water. The solvent was removed from the dried organic layer and the residue was distilled to afford **6f** (14.2 g, 76%): bp 66–69 (20 mmHg); MS (*m*/*e*) 150 (M^+, 17%), 110 (10%), 109 (100%), 83 (17%); ^{1}H NMR ($CDCl_3$) δ 2.0–2.8 (4 H, m), 4.6–5.0 (2 H, m), 5.2–6.0 (1 H, m), 6.5–7.1 (4 H, m); IR (film) 1640, 1590, 1495, 1455, 1235, 910, 755 cm^{-1}. This compound was shown to be homogeneous by GLC (column A, 70 and 50 °C).

***o*-(3-Butenyl)bromobenzene (6b).**[42] To the Grignard reagent prepared similarly from *o*-bromobenzyl bromide (25 g) and magnesium (2.9 g) in ether (80 mL) was added allyl bromide (14.5 g) dropwise. The mixture was boiled under reflux for 20 h and the product, bp 53–55 ° 0.5 mmHg), was isolated as in the previous case. Yield: 9.1 g (43%). A minor impurity (ca. 7%) was removed by flash chromatography on silica gel (hexane). MS (*m*/*e*) 212, 210 (M^+, 1:1, 2%), 171 (95%), 169 (100%), 131 (65%), 130 (31%), 90 (41%), 89 (34%), 77 (15%), 63 (23%); ^{1}H NMR ($CDCl_3$) δ 2.0–2.5 (2 H, m), 2.5–2.9 (2 H, m), 4.6–5.0 (2 H, m), 5.3–6.1 (1 H, m), 6.5–7.4 (4 H, m); IR (film) 1640, 1565, 1470, 1440, 1030, 920, 755 cm^{-1}. Anal. Calcd for $C_{10}H_{11}Br$: C, 56.90; H, 5.25. Found: C, 57.30; H, 5.44. MS for exact mass: calcd for M^+ 210.0045, found 210.0056.

General Reaction Procedure. Ammonia was distilled from sodium into a 250-mL three-necked flask containing *tert*-butyl alcohol (33 mL) and equipped with a dry ice condenser and stirring bar, until the total volume of solution in the flask reached approximately 100 mL. The halo compound (10 mmol) was then added by syringe. While the reaction mixture was kept at reflux under a nitrogen atmosphere, lumps (ca. 2 mmol) of potassium (to a total of 20 mmol) were successively added to the stirred solution. Each lump was added after the previous one had reacted. After the addition was complete, the mixture was stirred for 2 min. Ammonium nitrate (ca. 2 g) was slowly added, the mixture was diluted with diethyl ether (100 mL), which had been chilled to below −40 °C, and the ammonia was then allowed to evaporate as the apparatus warmed to room temperature over several hours. Water (100 mL) was added, the mixture was stirred, and the organic phase was separated. The ether layer was washed further with water (2 × 100 mL) and dried. After the addition of an internal standard (*tert*-butylbenzene, 10 mmol), the mixture was analyzed by GLC. For the quantitation of **4** and **5**, benzene was used as an internal standard (column B, 70 °C); all other products were determined on column A at various temperatures. Except for **11** and 1,2-bis(1-indanyl)ethane (**12**), products were identified by comparison of their GLC retention times and mass spectral fragmentation patterns with those of authentic samples. In experiments with 6-bromo-1-hexene, the total material balance was less than 100%. Other products were not detected by GLC to account for the deficiency. Although evaporation of the ammonia was carefully controlled to avoid excessive losses of the volatile **4** and **5**, the evaporation of ammonia solutions containing known amounts of **4** and **5**, with experimental conditions being reproduced as closely as possible, demonstrated that ca. 21% of **4** and **5** were lost. Importantly, however, the ratios of **4** and **5** were shown to remain quite constant; there was no preferential evaporation of either.

1-Methylidan (11). The products from the reaction of **6i** with potassium in liquid ammonia/*tert*-butyl alcohol were distilled (60–90 °C (19 mmHg)) to separate them from the dimer. The distillate was then subjected to HPLC to afford a small sample of **11**: MS (*m*/*e*) 132 (M^+, 44%), 117 (100%), 115 (38%), 91 (28%); ^{13}C NMR ($CDCl_3$) δ 20.0 (q), 31.5 (t), 34.8 (t), 39.6 (d), 123.2 (d), 124.4 (d), 126.1 (d), 143.8 (s), 148.7 (s); ^{1}H NMR ($CDCl_3$) δ 1.31 (3 H, d, $J = 7$ Hz), 1.5–1.8 (1 H, m), 2.1–2.5 (1 H, m), 2.7–3.0 (2 H, m), 3.0–3.4 (1 H, m), 7.19 (4 H, "s").

1,2-Bis(1-indanyl)ethane (12). The volatile products from the reaction of **6i** with potassium in NH_3/*t*-BuOH were removed by evaporation in vacuo (the pressure being decreased slowly to 0.1 mm and the temperature increased to 100 °C). After preliminary purification by flash chromatography on silica gel (2% CH_2Cl_2/hexane), the semicrystalline mixture was subjected repeatedly to HPLC (silica gel–hexane) to afford pure samples of two components. The first eluted remained an oil: ^{13}C NMR ($CDCl_3$) δ 31.7 (t), 32.3 (t), 33.1 (t), 45.1 (d), 123.1 (d), 124.6 (d), 126.3 (d), 144.1 (s), 147.7 (s); ^{1}H NMR ($CDCl_3$) δ 1.2–2.5 (8 H, m), 2.6–3.4 (6 H, m), 6.88 (8 H, "s"); MS (*m*/*e*) (20 eV) 262 (M^+, 28%), 132 (19%), 130 (10%), 119 (15%), 118 (11%), 117 (100%), 86 (16%), 84 (25%). The second eluted compound crystallized on standing: mp 93–94 °C; ^{13}C NMR ($CDCl_3$) δ 31.6 (t), 32.4 (t), 33.2 (t), 45.3 (d), 123.7 (d), 124.5 (d), 126.2 (d), 144.0 (s), 147.6 (s); ^{1}H NMR ($CDCl_3$) δ 1.2–2.5 (8 H, m), 2.5–3.3 (6 H, m), 6.87 (8 H, m); MS (*m*/*e*) 262 (M^+8 26%), 132 (20%), 130 (5%), 119 (16%), 118 (11%), 117 (100%). Anal. (on mixture of diastereomers) Calcd for $C_{20}H_{22}$: C, 91.55% H, 8.45. Found: C, 91.76; H, 8.39. MS for exact mass (*m*/*e*): calcd for M^+ 262.1722, found 262.1731.

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Registry No. 1, 2695-47-8; **4**, 592-41-6; **5**, 96-37-7; **6b**, 71813-50-8; **6c**, 3047-25-4; **6f**, 71813-51-9; **6i**, 24892-64-6; **10**, 768-56-9; **11**, 767-58-8; **12**, 102396-14-5; K, 7440-09-7; Na, 7440-23-5; Li, 7439-93-2; *o*-fluorobenzyl chloride, 345-35-7; allyl bromide, 106-95-6; *o*-bromobenzyl bromide, 3433-80-5; 1,11-dodecadiene, 5876-87-9.

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