which are of importance with respect to obtaining sets of π electron acceptor (+R) substituents having a high degree of nonlinearity between the σ_I and $\sigma^0{}_R$ values. Values of C_p-SCS and σ_I for these substituents and the $\sigma^0{}_R$ values defined by these results are given in Table VI.

Registry No. *N*,*N*-Dimethylaniline, 121-69-7; aniline, 62-53-3; anisole, 100-66-3; phenyl ether, 101-84-8; fluorobenzene, 462-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; toluene, 108-88-3; benzene, 71-43-2; methyl phenyl sulfoxide, 1193-82-4; α,α,α-trifluorotoluene, 98-08-8; benzophenone, 119-61-9; benzonitrile, 100-47-0; acetophenone, 98-86-2; ethyl benzoate, 93-89-0; phenyl sulfone, 127-63-9; methyl phenyl sulfone, 3112-85-4; nitrobenzene, 98-95-3; benzaldehyde, 100-52-7; 2,2,2-trifluoroacetophenone, 434-45-7; α-oxobenzeneacetonitrile, 613-90-1.

Influence of Steric Factors in the E2 Reaction. Calculation of Nonbonded Interactions and Minimum-Energy Trajectories for Base Approach in the E2 Reaction of Some Simple Alkyl Systems

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Results are presented for the evaluation of nonbonded interactions in the E2 reaction of several simple alkyl halide substrates. Minimum-energy trajectories of the base as it approaches the labile hydrogen are determined by using a Lennard-Jones 6/12 potential to describe the nonbonded interactions. These calculations are summarized as the repulsive force the base encounters when it is at its van der Waals radius from the labile hydrogen. These forces allow direct comparison of systems where isomeric reactions are possible as ratios of repulsive forces for the isomeric reaction geometries. Comparisons are made with bases of three different sizes (van der Waals radii = 3, 10, and 20 Å) and by their interactions with alkyl substrates with various alkyl substitution patterns (R = H, Me, Et, *i*-Pr, Pr, *t*-Bu, and Bu) around the E2 reaction center. These results establish a qualitative guide in succinctly stating the steric requirement of a base or departing leaving group in the E2 reaction.

Most base-promoted β-elimination reactions have been classified into the broad categories of E1, E1cB, or E2. These classifications have implied specific reaction pathways, and the general descriptions for these modes of reaction have been used to rationalize the orientational product selection for elimination reactions which yield the Hofmann and/or Saytzev alkenes.[1] Elimination reactions classified as E2, with the synchronous, antiperiplanar departure of both units of the molecule being eliminated, have been the focus of recent experimental and theoretical interest.[2] The goal of these investigations has been to understand and assess the factors which determine the product distribution in systems where there can be a selection between different isomeric E2 reaction pathways.

The base-promoted dehydrohalogenation of 2-alkyl halides is perhaps one of the most direct examples of the E2 reaction. In fact, the study of the various halide analogues in the 2-hexyl series by Bunnett has provided the foundations of the variable transition state theory.[3] In this theory, the amount of alkene character present at the transition state is specified as the determining factor in product selection. This description has been extremely successful in utilizing the relative thermodynamic stabilities of the isomeric alkene products as the primary predictors to explain qualitatively the orientational and geometrical selection between isomeric reaction pathways that are possible in these reactions. However, in several elimination reactions involving 2-alkyl halides and 2-alkyl arenesulfonates there have been product distributions reported that require the consideration of other experimental factors as modifiers to the amount of alkene character present in the transition state.[4-6] Even in the dehydrohalogenation of 2-halobutanes, changes in experimental parameters such as solvent, base size, and base strength have yielded product distributions that are inconsistent with the thermodynamic stabilities of the corresponding alkenes.[7]

One of the most obvious experimental factors that can modulate the relative free energies of isomeric reaction pathways is the distinctly different nonbonded interactions imposed by the different molecular geometries required for reactions leading to the isomeric products. These steric factors, associated with base size and the dimension and conformation of the leaving group, have been employed to explain changes in product distributions for many different systems.[7-9] Since it is the overall difference in free energy change that dictates the product selection, the steric factor must be assessed for the geometries required by each isomeric reaction pathway. Also, the change in free energy associated with steric influences is a duality of enthalpy and entropy, and even a very qualitative un-

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derstanding of this composite is often hard to establish. Any evaluation of how steric factors influence the relative free energy differences of isomeric reaction coordinates must have some guide to the sensitive relationship between enthalpy and entropy.[10]

In simple systems, where the size of the base is clearly the primary factor, the consideration of a steric influence exclusively in terms of enthalpy has been quite successful.[8] However, in more complex systems, where entropy considerations are important or where there are simultaneous steric contributions associated with the leaving group and the attacking base, the separate contributions of enthalpy and entropy are less clear.[7,11]

In order to have a qualitative guide for the division of a steric effect into the components of enthalpy and entropy for the E2 reaction, we have calculated minimum-energy trajectories for bases of varying sizes as they approach the labile hydrogen in several alkyl systems arranged to be compatible with geometries required for E2 reactions. Although geometries of the alkyl groups with sp^3 carbons are used to evaluate the nonbonded interactions with the base, these interactions are at least a beginning toward the complete description of the reaction coordinate. The energies were calculated by using a Lennard-Jones 6/12 potential to describe the nonbonded interactions (eq 1),

$$E_{\mathrm{nonbonded}} = \epsilon[(r^*/r)^{12} - 2(r^*/r)^6] \quad (1)$$

where $\epsilon = 0.2$ kcal, r^* is the sum of the van der Waals radii for the two interacting spherical domains (all carbon units of the alkyl framework were considered as "superatoms" with van der Waals radii of 2.0 Å), and r is the distance between the centers of the interacting domains.[12,13] The sums of the interactions of the base and the carbon units of the alkyl groups involved in the E2 reaction provide a comparitive scale for the analysis of experimental results. They represent an evaluation of the enthalpy contribution to the steric requirement for both the attacking base and/or the departing leaving group. A direct comparison can be made for a series of alkyl substrates reacting with a base of constant size or for a specific alkyl substrate reacting with a series of differently sized bases. This steric interaction is summarized as the repulsive force for each trajectory evaluated when the base is at its van der Waals radius from the labile hydrogen. These repulsive forces then allow a direct and succinct comparison of repulsive interactions.

Calculations

The framework of the molecule undergoing elimination is arranged with the hydrogen and the leaving group in an antiperiplanar orientation by using standard sp^3 carbon bond lengths and bond angles.[14] The specific alkyl structure is placed in a Cartesian coordinate system with the labile hydrogen at the origin and the C_α–C_β bond in the xz plane parallel with the x axis above the xy plane. The positions of the attacking base are restricted to a hemisphere about the origin of specified radius and below the xy plane. The position of the base on the surface of the hemisphere is changed by incrementing the spherical polar angles θ and ϕ over the ranges of 90–180° and 0–360°, respectively. The total nonbonded interaction for each position of the base on the hemisphere is calculated as the sum of the interactions of the base with each of the carbon units in the alkyl substrate by using a Lennard-Jones 6/12 potential to describe the individual interactions. The minimum of the total nonbonded interactions for the θ and ϕ increments is representative of one point in the trajectory of the base which is best in terms of steric interactions. The distance of the base from the origin is incremented and the process repeated so that the optimum path of the attacking base may be plotted as it approaches the labile hydrogen.

Computer programs that evaluate the total nonbonded interaction and generate a minimum-energy trajectory have been written in both Fortran IV and APL-PLUS.[15] The programs were implemented on an IBM 370/125 computer and an Amdahl 400 computer accessed via a Scientific Time Sharing terminal. The input required for these programs includes the Cartesian coordinates for the carbons in the substrate, the energy factor for each carbon (ϵ), and the distances from the origin over which the minimum-energy trajectory is to be calculated. The result of the calculation gives the minimum energy and coincident coordinates for the base at each incremental radius in the trajectory along with the slope of the potential at the van der Waal radius of the base.

In many systems the orientational requirement imposed by the stereochemical restrictions of the E2 elimination center does not preclude all units of the carbon framework from enjoying free rotation about carbon–carbon bonds. There are often several conformations that must be considered for the alkyl groups substituted around the reaction center. The energy factor, ϵ, provides a convenient parameter for weighting each of the contributing conformations that are included for a specific carbon atom. It should be noted that when an individual carbon has several orientations due to bond rotation, the ϵ from eq 1 can be divided over these orientations to allow scaling of rotamers; however, the sum of this apportionment of ϵ must always equal 0.2 kcal for a specific carbon regardless of the number of rotamers considered. In these calculations only gauche and anti conformations are included where free rotation is possible, and since the effect of the leaving group creates some uncertainty as to the weighting of these conformations, each was considered equally.[16]

The calculated minimum-energy potentials are comparable directly only if the size of the base is held constant, since a change in the size of the base makes the potential "harder" or "softer".[17] Even if the comparison is restricted directly to a constant base size, a full and complete analysis of these results would require a tedious point by point comparison of the calculated potentials. In order to simplify this comparison and to succinctly and consistently state the repulsive interaction, we evaluated a repulsive force for each potential at the van der Waals radius of the base. The magnitude of this repulsive force represents the relative steepness of the repulsive potential.

$$\text{repulsive force} = \partial E_{\mathrm{nonbonded}}/\partial r$$

The limitation on the comparison of the repulsive forces can be overcome by comparing the relative ratios of these repulsive forces for reactions which have isomeric orientations for elimination.

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Table I

entry no.	reactant	product	R_1	R_2	R_3	R_4	θ, deg	ϕ, deg	repulsive force at certain van der Waals radii, kcal/Å		
									3 Å	10 Å	20 Å
1	EtX	ene	H	H	H	H	143	180	−4.94	−0.234	−0.0521
2	1-X-Pr	ene	H	Me	H	H	151	206	−5.09	−0.272	−0.0657
3	1-X-Bu	1-ene	H	Et	H	H	152	224	−5.15	−0.294	−0.0711
4	1-X-3-MeBu	1-ene	H	*i*-Pr	H	H	151	235	−5.19	−0.303	−0.0727
5	1-X-Pe	1-ene	H	Pr	H	H	150	242	−6.55	−0.381	−0.0790
6	1-X-3,3-Me$_2$Bu	1-ene	H	*t*-Bu	H	H	151	241	−5.22	−0.306	−0.0726
7	EtX	ene	H	H	H	H	143	180	−4.94	−0.234	−0.0521
8	2-X-Pr	ene	H	H	H	Me	132	192	−5.02	−0.252	−0.0576
9	2-X-Bu	1-ene	H	H	H	Et	123	198	−6.27	−0.293	−0.0625
10	2-X-3-MeBu	1-ene	H	H	H	*i*-Pr	118	201	−6.83	−0.311	−0.0646
11	2-X-Pe	1-ene	H	H	H	Pr	115	204	−12.5	−0.409	−0.0725
12	2-X-3,3-Me$_2$Bu	1-ene	H	H	H	*t*-Bu	114	203	−7.23	−0.327	−0.0660
13	2-X-Hex	1-ene	H	H	H	Bu	109	208	−60.4	−0.590	−0.0877
14	2-X-Pr	1-ene	H	H	H	Me	132	192	−5.02	−0.252	−0.0576
15	2-X-Bu	cis-2	H	Me	H	Me	139	209	−5.17	−0.293	−0.0722
16	2-X-Pe	cis-2	H	Et	H	Me	142	222	−5.23	−0.321	−0.0800
17	2-X-4-MePe	cis-2	H	*i*-Pr	H	Me	143	230	−5.27	−0.333	−0.0830
18	2-X-Hex	cis-2	H	Pr	H	Me	142	235	−6.65	−0.416	−0.0900
19	2-X-4,4-Me$_2$Pe	cis-2	H	*t*-Bu	H	Me	143	235	−5.31	−0.340	−0.0843
20	2-X-Pr	ene	H	H	H	Me	132	192	−5.02	−0.252	−0.0576
21	2-X-Bu	trans-2	Me	H	H	Me	142	174	−5.21	−0.332	−0.0855
22	2-X-Pe	trans-2	Et	H	H	Me	148	162	−5.30	−0.406	−0.1060
23	2-X-4-MePe	trans-2	*i*-Pr	H	H	Me	148	152	−5.37	−0.453	−0.120
24	2-X-Hex	trans-2	Pr	H	H	Me	148	146	−7.30	−0.632	−0.138
25	2-X-4,4-Me$_2$Pe	trans-2	*t*-Bu	H	H	Me	149	147	−5.43	−0.488	−0.129
26	1-X-Pr	ene	H	Me	H	H	151	206	−5.09	−0.272	−0.0657
27	2-X-Bu	cis-2	H	Me	H	Me	139	209	−5.17	−0.293	−0.0722
28	3-X-Pe	cis-2	H	Me	H	Et	130	212	−6.46	−0.350	−0.080
29	3-X-2-MePe	cis-2	H	Me	H	*i*-Pr	125	213	−7.06	−0.377	−0.0819
30	3-X-Hex	cis-2	H	Me	H	Pr	122	215	−12.6	−0.472	−0.0903
31	3-X-2,2-Me$_2$Pe	cis-2	H	Me	H	*t*-Bu	121	214	−7.48	−0.392	−0.0847
32	1-X-Pr	ene	Me	H	H	H	151	154	−5.09	−0.272	−0.0657
33	2-X-Bu	trans-2	Me	H	H	Me	142	174	−5.21	−0.332	−0.0855
34	3-X-Pe	trans-2	Me	H	H	Et	134	182	−6.91	−0.468	−0.108
35	3-X-2-MePe	trans-2	Me	H	H	*i*-Pr	130	186	−7.68	−0.547	−0.124
36	3-X-Hex	trans-2	Me	H	H	Pr	129	190	−16.9	−0.735	−0.139
37	3-X-2,2-Me$_2$Pe	trans-2	Me	H	H	*t*-Bu	127	189	−8.24	−0.606	−0.136
38	1-X-Bu	1-ene	H	Et	H	H	152	224	−5.15	−0.294	−0.0711
39	2-X-Pe	cis-2	H	Et	H	Me	142	222	−5.23	−0.321	−0.080
40	3-X-Hex	cis-3	H	Et	H	Et	133	223	−6.58	−0.392	−0.089
41	1-X-Bu	1-ene	Et	H	H	H	152	136	−5.15	−0.294	−0.0711
42	2-X-Pe	trans-2	Et	H	H	Me	148	162	−5.30	−0.406	−0.106
43	3-X-Hex	trans-3	Et	H	H	Et	140	172	−7.43	−0.654	−0.148

Results and Discussion

The results of the calculations are summarized in Table I. These results include the angular approach of minimum energy for several alkyl substrates and the repulsive force as calculated at the van der Waals radius of the bases. The relative placement of the alkyl groups around the E2 reaction center is shown in Figure 1. These results show several qualitative trends associated with base size and the substitution at the α (R3 and R4) and β (R1 and R2) carbons.

The angular path of the minimum-energy trajectory in Table I is given for the largest base. These trajectories represent the minimum-energy approach only when the steric interaction is predominantly repulsive. Without the consideration of steric factors, the optimum approach of the attacking base would be in the xz plane, colinear with the carbon–hydrogen bond that is broken (θ = 160.5° and ϕ = 180°). However, as alkyl groups are added to the α and β carbons, the approaching base is pushed out of the xz plane. The results show a similar pattern with the optimum angle ϕ being changed from 180° (approach in the xz plane) by the substitution at the α and β carbons. In Table I entries 1–6 and 7–13 represent changing the β and α substitution, respectively. It is clear from these results that the change in α has a larger effect in terms of angular adjustment on θ than it does on ϕ, while there is a larger angular adjustment in ϕ than in θ when the β substitution is changed. This same generalization is also consistent with the observations summarized in entries 14–19, 20–25, and 26–31. However, as the alkyl substituents become larger, the effect is reduced, and the major angular adjustment for the trans geometry is always in ϕ

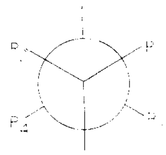

Figure 1. Generalized description of groups used for trajectory calculations. See the text for their placement in a Cartesian coordinate system.

(entries 32–37 and 41–43) while the major angular adjustment is in θ for the cis geometry (entries 26–31 and 38–40). The angular trajectories reported in entries 14–19 and 20–25 are consistent with the qualitative description of the minimum-energy approach of large bases that has been proposed by Bartsch.[8]

The repulsive forces that are reported in Table I are comparable only for a base of the same size. It is clear by comparing the forces for bases of different sizes that this comparison only reflects the "hardness" or "softness" of the potential as it is dependent upon base size. Since the representation of the enthalpy is dependent on the choice of the potential (i.e., the relative steepness of the potential), the direct comparison of potentials or forces must be restricted to a series of the same base size. A qualitative comparison between differently sized bases is possible by examining the ratios of the forces. Comparing entries 15 and 21 in Table I, the steric interaction calculated for the formation of *cis*- and *trans*-but-2-ene may be compared as the ratio of forces for bases of different sizes. With a relatively small base (van der Waals radius = 3 Å) the cis/trans ratio of the forces is 0.99, while the ratio of forces for a large base (20 Å) is 0.84. This is consistent with the larger base having a more selective steric effect, and on the basis of steric considerations the reaction to yield the cis configuration is favored by a large base. In general, the cis/trans ratio of forces in all substrates is near 1.0 for small bases and is less for large bases with the exception of entries 30 and 36 as well as entries 40 and 43. In these instances the ratios are less than 1.0 even for small bases; however, in both cases the ratios are still smaller for large bases.

Another qualitative feature that is shown by these results is the increase in repulsive force as the size of the alkyl substituent is increased. Table entries 1–6 show an increase in the repulsive force, H < Me < Et < *i*-Pr < *t*-Bu < Pr, for β substitution with the attack of small bases. As the size of the base is increased, the substituents Et, *i*-Pr, and *t*-Bu become nearly equivalent. Entries 7–13 show the same effect with a change in substitution at the α carbon. The effects of the α substitution are extended to include substitution at the α carbon with a butyl group (entry 13). Although the relative ordering of the repulsive force remains the same, the effect for interaction with a small base is far more dramatic, particularly the large increase in repulsive force going from Et to Pr and from Pr to Bu and the near equivalence of the forces for Et, *i*-Pr, and *t*-Bu. The effect of changing the α substituent on the trajectories calculated for the interaction with a large base reduces the differentials of the repulsive forces for the substituent changes. These results can be qualified into two different components: (1) the chain-length effect and (2) the group-bulk effect.

The group-bulk effect can be envisioned as a diffuse steric interaction. All carbon units in the substituent contribute more or less equally to the total steric repulsion. The interference of the group-bulk effect is nonspecific. In a chain-length effect it is the terminal carbon in the chain that is primarily responsible for the steric repulsion. The chain can rotate so as to position this carbon for a specific and focused interaction with the base. Clearly the chain-length effect is always important; however, it is totally dominant for steric interactions with small bases. As the size of the base increases the group-bulk effect becomes increasingly important. As noted earlier the calculations include several different conformations for systems in which there is the possibility of free rotation within the alkyl substituent. As the length of the alkyl chain is increased there is more flexibility for the rotation of the alkyl group into a conformation that places the terminal carbon close to the labile hydrogen. These conformations contribute strongly with a very unfavorable steric interaction and account for large increases in the repulsive force as the substituent is changed from ethyl to propyl and from propyl to butyl (chain-length effect). This effect is most noticeable for small bases and is moderated as the size of the base is increased. An entropic sacrifice by the alkyl substrate in the restriction of some of the rotations which yield these unfavorable conformers can reduce the large differential in repulsive forces. When the attacking base is large, the entropic sacrifice of the system will not yield the same benefit since the bulk of the alkyl group becomes more important in determining the steric effect.

One particularly interesting observation regarding this aspect of the chain-length effect comes from entries 13, 18, and 24 in Table I. These data allow the comparison of the enthalpic contribution of the steric interaction to the free energy of the three isomeric transition states in the dehydrohalogenation of 2-halohexane. Bartsch predicts trans 2-ene > cis 2-ene > 1-ene for the steric repulsion of a base approaching the labile hydrogen.[8] For the large base we see that the data are in agreement with this prediction. However, for a small base where chain effects are important, the transition state leading to the Hofmann alkene is the most repulsive by a significant amount. If several particularly repulsive rotational conformations are removed from the calculation, the chain effect is no longer operant and the repulsive forces fall back into line with the prediction.

There are experimental observations that have been interpreted to associate the steric factor with a preference for the Hofmann product.[8] Since the calculated enthalpic input into the free energy of the transition state is unfavorable, it must be the case that entropy is being sacrificed to avoid the steric repulsion of the particular rotamer in order to achieve a favorable enthalpy. A kinetic study is currently underway to investigate this hypothesis. The work of Bartsch and Bunnett lends support to this concept of an entropy–enthalpy trade-off.[3]

The results in Table I also allow a comparison of the repulsive forces between substrates with the alkyl substitution at the α and β carbons (except for methyl). These data show that the repulsive force is larger when the substitution is at the α carbon as long as the attacking base is small or intermediate in size. However, when the base is large, the substitution at the β center becomes more of a problem (see entries 3 and 9, 4 and 10, 5 and 11, and 6 and 12).

There are two interacting features which account for this observed trend. It might be expected that the α substituent would be more repulsive than the β because it sits lower in the xz perspective. However, it is also true that the α substituent is insulated from the labile hydrogen (point of base attack) by one more carbon than is the β group. For small- and intermediate-sized bases we see that β substitution is more favorable. This is probably because the bulk or chain-length effect of the α substituent is large enough to overcome the extra insulation, while the β substituent, although less insulated, enjoys a positional advantage above the xy plane.

When the base is large (20 Å), the β substitution is the more repulsive. This is due to the fact that the large base negates the positional advantage of the β group, and since it is less insulated, it is now the more repulsive.

The descriptions to this point have been of base attack; however, these trajectories are also qualitatively useful to assess the steric requirement of the departing leaving group. A reversal of the trajectories will describe the optimum path of a leaving group if appropriate entries in Table I are compared. For example, entry 16 represents formation of *cis*-pent-2-ene from 2-halopentane, and entry 28 represents the steric requirements of the halogen as it departs. The summary of this relationship involves the interchange of substituents R_1/R_3 and R_2/R_4. Again these comparisons are qualitative; however, they do represent a beginning for the establishment of a quantitative description of steric effects in the E2 reaction.

Conclusion

Computer-generated minimum-energy base trajectories for E2 reactions have been presented. A comparison of the repulsive forces yields several useful qualitative observations. The attack trajectories are consistent with what one would expect from examination of molecular models. The increase in repulsive force with increased chain length and steric bulk of alkyl substituents allows a distinction to be made between two types of steric interaction: the chain-length effect and the group-bulk effect.

The trajectories also have implications for the relative stabilities of α and β alkyl substitution. With small and intermediate sized bases the β position offers less interference to the approaching base. Large bases encounter less difficulty with an α substituent. This is probably due to a shift in importance of the groups being removed from the reaction center in the perspective and being removed via carbon insulation, since the interactions are dependent only on distance.

Most importantly, the calculations give some insight into the relative steric repulsion a base encounters when it approaches the isomeric conformations for a dehydrohalogenation. For intermediate and large bases the results are in accord with what would be expected from simple observation 1-ene < cis < trans. With small bases, however, the transition state leading to the Hofmann alkene offers a significantly increased relative steric repulsion due to a chain effect from particular rotational conformations. Removal of these rotamers restores the expected order of stability. This behavior is indicative of an entropy–enthalpy trade-off that operates to minimize the free energy of the transition state.

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Registry No. EtBr, 74-96-4; ethene, 74-85-1; propene, 115-07-1; 1-butene, 106-98-9; 3-methyl-1-butene, 563-45-1; 1-pentene, 109-67-1; 3,3-dimethyl-1-butene, 558-37-2; 1-hexene, 592-41-6; *cis*-2-butene, 590-18-1; *cis*-2-pentene, 627-20-3; *cis*-4-methyl-2-pentene, 691-38-3; *cis*-2-hexene, 7688-21-3; *cis*-4,4-dimethyl-2-pentene, 762-63-0; *trans*-2-butene, 624-64-6; *trans*-2-pentene, 646-04-8; *trans*-4-methyl-2-pentene, 674-76-0; *trans*-2-hexene, 4050-45-7; *trans*-4,4-dimethyl-2-pentene, 690-08-4; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8.

Elimination and Substitution in the Reactions of Vicinal Dihalides and Oxyhalides with Trimethylstannylsodium. Effects of Solvent and of Ion Aggregation on Course and Stereochemistry

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The course and stereochemistry of the reactions of vicinal dihalides and vicinal oxyhalides with trimethylstannylsodium have been studied in THF and in other solvents. Cation solvating agent effects have also been examined. The vicinal dihalides react uniformly via anti stereochemistry to produce the corresponding alkenes in nearly quantitative yields. 2-Bromo-3-methoxybutane yields both elimination and substitution (2-methoxy-3-(trimethylstannyl)butane) products. The stereochemistry is predominantly syn when THF is the solvent, and elimination predominates. When TG is the solvent, substitution occurs as the predominant reaction; the stereochemistries of both substitution and elimination are nonspecific. The mechanistic implications of these observations are considered.

Studies on the scope and mechanisms of vicinal dehalogenations and related elimination reactions have been reported sporadically since the observation of the iodide-induced debromination of coumarin dibromide by Perkin.[1] Among the agents which have been shown to bring about these reactions are metals such as sodium in liquid ammonia[2,3] or tetrahydrofuran,[4] magnesium,[5,6] zinc,[4,6a] cadmium,[5] lithium,[6a] and sodium naphthalenide,[7,8] electrolysis,[9,10] subvalent metal ions such as Fe(II),[5] Sn(II),[5,11] Cr(II),[5,6,12,13] Pt(II),[5] Co(II),[14] $Fe(CO)_2CpNa$, and Ti(II),[16] free

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