

absence of vinyl proton resonances in the  $\delta$  5-7 region. GLC analysis showed only minor amounts of the expected alcohol product; most of the material did not elute out of the column. Photolysis of 1-(*p*-bromophenyl)ethanol, the expected photohydration product, under similar irradiation times as for 8 also resulted in extensive photopolymerization.

(e) *m*-(Trifluoromethyl)styrene (11). A solution of 60 mg of 11 (130 mL CH<sub>3</sub>CN and 400 mL ~10% H<sub>2</sub>SO<sub>4</sub>) was irradiated (after outgassing with argon) at 254 nm for 18 h. After workup, the photosylate was analyzed by GC, which showed six major products (~97% conversion), one of which (~20%) was the expected alcohol. No attempts were made to identify the other products. Irradiation of 1-(*m*-(trifluoromethyl)phenyl)ethanol, the expected alcohol product, under identical conditions as for

11, resulted in >95% recovery of the material. This experiment shows that the alcohol product, once formed, does not undergo secondary photochemistry. Thus it strongly suggests that other primary photochemical processes are competing with photo-protonation for 11.

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**Registry No.** 3, 100-42-5; 4, 637-69-4; 5, 622-97-9; 6, 405-99-2; 7, 350-51-6; 8, 2039-82-9; 9, 1073-67-2; 10, 3435-51-6; 11, 402-24-4; 12, 100-13-0; 13, 586-39-0; 14, 827-54-3.

## Complex-Base-Promoted Syn Eliminations from *trans*-1-Bromo-2-chlorocyclohexane<sup>1</sup>

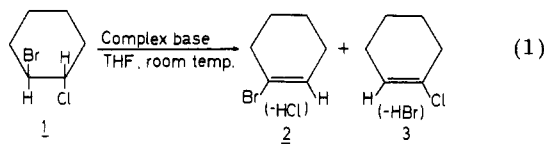
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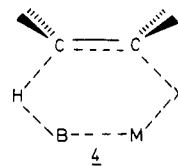
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Syn eliminations from *trans*-1-bromo-2-chlorocyclohexane (1) induced by complex-base combinations of NaNH<sub>2</sub>-NaOR(Ar) in tetrahydrofuran at room temperature favor dehydrochlorination (54-65%) over dehydrobromination. Under the heterogeneous reaction conditions, oxyanion bases derived from tertiary, secondary, and branched primary alcohols as well as phenols and 2-butanone are effective complex-base components, which suggests that NaNH<sub>2</sub> is the effective base species. Reactions of 1 with NaNH<sub>2</sub>-NaO-*t*-Bu are not influenced by ultrasonic irradiation, but the propensity for loss of the normally poorer leaving group disappears in the presence of 15-crown-5. Transition states for complex-base-promoted syn eliminations are discussed.

Lee and Bartsch<sup>2</sup> have reported a reversal of the usual E2 leaving group ordering<sup>3,4</sup> for syn eliminations from several *trans*-1,2-dihalocycloalkanes induced by the complex base<sup>5</sup> NaNH<sub>2</sub>-NaO-*t*-Bu. Thus, when treated with NaNH<sub>2</sub>-NaO-*t*-Bu in tetrahydrofuran (THF) at room temperature for 24 h under heterogeneous conditions, *trans*-1-bromo-2-chlorocyclohexane (1) yielded 52-55% of 1-bromocyclohexene (2) and 30-31% of 1-chlorocyclohexene (3; eq 1). Analogous syn elimination from



*trans*-1-bromo-2-fluorocyclohexane gave 85% of 1-bromocyclohexene (dehydrofluorination product) but no detectable 1-fluorocyclohexene (dehydrobromination product). The preferential loss of the normally poorer halogen leaving group in these syn eliminations was rationalized by Sicher's transition-state 4<sup>6</sup> in which there is strong interaction of the base counterion M with the leaving group X.



To provide further insight into these unusual syn elimination reactions, we have examined the effects of added crown ether, ultrasonic irradiation, and oxyanion component variation within the complex base upon the relative yields of 2 and 3 in complex-base-promoted 1,2-eliminations from 1. In addition, a qualitative assessment of the influence of such variations upon the activity of the complex-base combinations as dehydrohalogenation agents was made. The results of this study are now reported.

### Experimental Section

**Materials.** Tetrahydrofuran (Matheson Coleman and Bell) was distilled from lithium aluminum hydride under nitrogen immediately before use. Sodium amide powder (Fisher Scientific) was transferred and weighed in a nitrogen-flushed dry bag. Reagent grade alcohols from several commercial sources were distilled before use. The 15-crown-5 (Aldrich) was used directly. Other reagent grade inorganic and organic chemicals were used as received. *trans*-1-Bromo-2-chlorocyclohexane (1) was prepared by reaction of cyclohexene, *N*-bromoacetamide, and 16% aqueous HCl at -5 to -10 °C.<sup>7</sup> Compounds 2 and 3 were available from earlier work.<sup>2,7</sup>

**Gas-Liquid Partition Chromatography.** GLC analysis was conducted with a Varian Aerograph Series 2400 FID gas chro-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Table I. Elimination Reactions of *trans*-1-Bromo-2-chlorocyclohexane Induced by  $\text{NaNH}_2\text{-Na}(\text{anion})$  in THF at Room Temperature

system	anion of Na(anion)	time required for for consumption of 1, h	% 2 <sup>a</sup> / (% 2 + % 3)	total yield of 2 + 3, <sup>b</sup> %
1	ethoxide	24	51	51
2	2-methylbutoxide	1	60	59
3	3-methylbutoxide	1	60	84
4	2-propoxide	1	60	64
5	3-methyl-2-butoxide	2	61	56
6	cyclohexoxide	1	54	68
7	<i>tert</i> -butoxide	2	65	87
8 <sup>c</sup>	<i>tert</i> -butoxide	0.5	3	76
9	2-methyl-2-butoxide	1	65	83
10	2,2,2-trifluoroethoxide	1	59	73
11 <sup>d</sup>	1,1,1,3,3,3-hexafluoro-2-propoxide	>24	64	33
12	phenoxide	1	62	80
13	<i>o</i> -methoxyphenoxide	1	60	69
14	<i>p</i> -methoxyphenoxide	1	61	81
15	enolate from 2-butanone	1	57	53
16	<i>tert</i> -butylthiolate	2	62	89
17	thiocyanate	1	55	57

<sup>a</sup> Standard deviation of  $\pm 1\%$  in repetitive analysis of reaction mixture. <sup>b</sup> Standard deviation of  $\pm 2\%$  from repetitive analysis of reaction mixture. <sup>c</sup> 15-Crown-5 was present in the reactant ratio of 1/ $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$ /15-crown-5 = 2:3:6. <sup>d</sup> Incomplete reaction after 24 h. Product data are for 24 h of reaction.

matograph with an oven temperature of 75 °C, using the following columns: column A, 5 ft  $\times$  1/8 in. of 5% SE-30 on Chromosorb P; column B, 10 ft  $\times$  1/8 in. of 20% SE-30 on Chromosorb P. For the analysis of 2 and 3, toluene was the internal standard, and molar response corrections were applied.

**Elimination from 1.** Under nitrogen, 9.8 mmol of  $\text{NaNH}_2$  was weighed into a 25-mL round-bottomed flask fitted with a reflux condenser. To the top of the reflux condenser was attached a T-tube through which a slow flow of nitrogen was passed during the reaction. The alcohol or other acidic substance (4.9 mmol) and 8.0 mL of dry THF were added to the flask, and the mixture was stirred magnetically for 1 h. After addition of 3.3 mmol of 1 to the stirred heterogeneous reaction medium at room temperature, the reaction was monitored by periodic removal of 2- $\mu\text{L}$  aliquots that were analyzed for unreacted 1 by GLC, using column A. When 1 had been consumed, the reaction mixture was poured into 70 mL of ice-water. The reaction flask was rinsed with a small amount of  $\text{Et}_2\text{O}$ . The rinsings and additional  $\text{Et}_2\text{O}$  (total of 30 mL) were added to the ice-water mixture. Toluene (internal standard) was added, and after being shaken, the flask was allowed to stand overnight in a refrigerator. The organic layer was then analyzed for 2 and 3 by GLC, using column B. Average values for the percentage of 2 and the percentage of 3 were calculated from at least analyses of the organic layer.

**Effect of Ultrasound.** The reaction of 1 with  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  was conducted as described above with the exception that the reaction flask was partially immersed in water in a Bransonic 220 ultrasonic cleaning bath.

**Control Experiments.** A complex base of  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  in THF was prepared in the usual fashion. Mixtures of 2 and 3 and, in some cases, added inorganic compounds were stirred with the complex base for 24 h at room temperature. The resulting mixtures were quenched, worked up, and analyzed for 2 and 3 as described above.

## Results

Selected data<sup>8</sup> for syn dehydrohalogenation of 1 induced by complex-base combinations of  $\text{NaNH}_2\text{-Na}(\text{anion})$  in THF at room temperature are presented in Table I. For each combination the relative percentage of 2 in the product mixture of 2 and 3, the total yield of 1-halocyclohexenes, and the approximate length of time required for consumption (less than 1% remaining) of 1 are given.

Reactions of 1 with  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  in THF have been repeated several times during a 3-year period by two different co-workers. Both the relative percentages of 2

and the total 1-halocyclohexene yields were found to be surprisingly reproducible ( $\pm 2\%$ ) for such a heterogeneous reaction system. In view of such reproducibility, only a single experiment was conducted for each complex-base component in the present study.

Control experiments revealed that the product 1-halocyclohexenes were partially decomposed to unidentified products when contacted with  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  in THF at room temperature for 24 h. Decomposition of 2 was somewhat more rapid than that of 3 and the decomposition of both 2 and 3 by this complex base was diminished in the presence of finely divided NaCl and NaBr.

A profound influence of 15-crown-5 upon the relative proportions of 2 and 3 formed in reactions of 1 with  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  is readily evident from a comparison of data for systems 7 and 8 in Table I. In the presence of crown ether the propensity for loss of the normally poorer leaving group disappears.

Data for eliminations from 1 promoted by complex-base combinations of  $\text{NaNH}_2\text{-NaS-}t\text{-Bu}$  and  $\text{NaNH}_2\text{-NaSCN}$  are also recorded in Table I.

## Discussion

Strong evidence that complex-base-promoted syn eliminations from *trans*-1,2-dihalocyclohexanes utilize transition states such as that depicted in 4 is provided by the effect of crown ether upon the competitive dehydrohalogenation pathways for 1. If interactions of the base counterion  $\text{Na}^+$  with the leaving group (M and X, respectively, in 4) are important, it would be predicted that the addition of a strong  $\text{Na}^+$  complexing agent should reduce, if not eliminate, these interactions. In agreement, the presence of 15-crown-5 diminishes the relative proportion of dehydrochlorination product from 65% to 3% in reactions of 1 with  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  (compare systems 7 and 8 in Table I). In the presence of 15-crown-5, the syn-elimination reaction exhibits the normal E2 reaction propensity for dehydrobromination over dehydrochlorination.<sup>3,4</sup>

Caubère and co-workers<sup>8</sup> have investigated the influence of varying the alkoxide component of the complex base upon the relative proportions of dehydrobromination and debromination in eliminations from *trans*-1,2-dibromocyclohexane. Our approach was to utilize the effects of anion component variations upon competitive dehydro-

(8) Additional data is provided as supplementary material.

chlorination and dehydrobromination of 1 to probe the nature of the actual elimination-promoting species in complex-base-induced syn eliminations.

Effects of varying the composition of the complex base were probed in heterogeneous reactions of 1 with 36 combinations of  $\text{NaNH}_2\text{-Na}(\text{anion})$  in THF at room temperature (Table I and ref 8). Results reveal the influence of the anion identity upon the amount and distribution of dehydrohalogenation products and provide a crude measure of the reactivity for different complex-base combinations.

The complex-base-promoted eliminations from 1 utilized an excess of base. Therefore, subsequent reactions of the 1-halocyclohexene products 2 and 3 with the excess base must be considered. In control experiments, stirring mixtures of 2 and 3 with  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  in THF at room temperature for 24 h caused partial decomposition of the 1-halohexenes to unidentified products. The decomposition of 2 was found to be somewhat more rapid than that of 3. Decompositions of the 1-halocyclohexenes by this complex base were diminished in the presence of finely divided NaCl and NaBr. This latter results suggests that in rapid (1–2 h) complex-base-promoted eliminations from 1 the colloidal NaCl and NaBr that are produced in the reaction deactivate the excess base and prevent the decomposition of the 1-halocyclohexene products. In agreement with this hypothesis, both the relative percentage of 2 and the total 1-halocyclohexene yield in reaction of 1 with  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  are the same when the reaction mixture is quenched after 2 h (system 7, Table I) and 24 h.<sup>2</sup> On the other hand, for slower elimination reactions of 1, the 1-halocyclohexene products are exposed to the active complex base for a prolonged period and some decomposition may occur.

Examination of the data for complex bases of  $\text{NaNH}_2\text{-Na}(\text{anion})$  in which the anion is an alkoxide reveals a pronounced influence of the alkoxide component upon the time required for consumption of 1 (Table I and ref 8). Alkoxide components derived from *n*-alcohols<sup>9</sup> uniformly gave slow reactions that required 20–30 h for completion. Due to this sluggishness, some decomposition of product 1-halocyclohexenes may have occurred (vide supra) and the data for the relative percentages of 2 and the total yields of 2 plus 3 for these systems must be viewed as possessing considerable uncertainty. On the other hand, when the alkoxide components were from branched primary alcohols,<sup>10</sup> secondary alcohols,<sup>11</sup> and tertiary alcohols,<sup>12</sup> the elimination reactions of 1 were complete in 2 h or less and the product data are considered to be reliable. For all of these systems, the relative percentages of dehydrochlorination product 2 lies within the range of 54–65%. Thus, for each of these complex bases dehydrochlorination is favored over the dehydrobromination of 1. Data for the combined yields of 1-halocyclohexenes exhibit considerably more variation. The major contributing factor to the less than quantitative yields of 1-halocyclohexenes is the concomitant dehalogenation reaction. Although GLC analysis indicated the presence of cyclohexene, the amounts of dehalogenation product were not determined. It has been previously established that

the relative proportions of dehydrohalogenation and dehalogenation products that are formed in eliminations from *trans*-1,2-dibromocyclohexane are quite sensitive to the identity of the alkoxide component of the complex base.<sup>13</sup> As a group, the alkoxide components derived from tertiary alcohols produced the highest yields of dehydrohalogenation products.

Recent research<sup>14,15</sup> has demonstrated remarkable rate enhancements when certain heterogeneous reactions are subjected to ultrasonic irradiation. For reactions of 1 with  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  in THF, modest increases in reactivity upon ultrasonication were found to be due to heating of the water in the ultrasonic cleaner to about 40 °C during the reaction. When parallel reactions of 1 with  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  in THF were conducted at 40 °C in the presence and absence of ultrasonic irradiation, the elimination product proportions and times required for the consumption of 1 were found to be the same.

In an attempt to probe the importance of electronic features of the alkoxide component in a complex base, reactions were conducted with alkoxides derived from 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoro-2-propanol (systems 10 and 11, respectively). Although preferential dehydrochlorination was again observed in both instances, the reactivities of such systems were surprisingly different from those noted with nonfluorinated alkoxide components. Thus, the complex base containing 2,2,2-trifluoroethoxide (system 10) underwent reaction with 1 much more rapidly than did the complex base derived from ethanol (system 1). In contrast, a complex base with 1,1,1,3,3,3-hexafluoro-2-propoxide as the alkoxide component (system 11) was very sluggish in comparison with that which contained 2-propoxide (system 4). The reasons for these contrasting reactivities are not understood at the present time.

Results obtained from reactions of 1 with complex bases of  $\text{NaNH}_2\text{-Na}(\text{anion})$  in THF at room temperature in which the anion is not an alkoxide are also presented in Table I. Effective complex bases may contain phenoxide ions (systems 12–14) and an enolate anion (system 15) but not carboxylate ions.<sup>8</sup> It was also found that the totally inorganic complex-base combination of  $\text{NaNH}_2\text{-NaSCN}$ <sup>16</sup> (system 17) was a reasonably effective reagent for producing syn dehydrohalogenation from 1. For all of these nonalkoxide-containing complex-base combinations, dehydrochlorination of 1 was favored over dehydrobromination.

Many reactions of strongly basic reagents have recently been found to proceed via one-electron-transfer processes.<sup>18,19</sup> To test for this possibility in complex-base-promoted dehydrohalogenation, the reaction of 1 with  $\text{NaNH}_2\text{-NaS-}t\text{-Bu}$  was conducted in THF at room temperature (system 16). The virtual identity of results for reactivity of the complex base, relative percentage of 2, and

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(16) Under similar conditions, complex-base combinations of  $\text{NaNH}_2\text{-NaNO}_2$ ,  $\text{NaNH}_2\text{-KSCN}$ , and  $\text{NaNH}_2\text{-NaCH}_2\text{CN}$  gave less than 2% of elimination from 1 after 4 h. Although  $\text{NaNH}_2\text{-NaCHPhCN}$  produced approximately 40% of dehydrohalogenation products in a reaction that was incomplete after 4 h, GLC analysis indicated the presence of several side products. Biehl and co-workers<sup>17</sup> have reported facilitation of benzene reactions by  $\text{NaNO}_2$ ,  $\text{NaSCN}$ ,  $\text{KSCN}$ ,  $\text{NaCH}_2\text{CN}$ , and  $\text{NaCHPhCN}$ .

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(9) Ethanol, 1-hexanol, 1-octanol, 1-decanol, 1-dodecanol, and 1-octadecanol.

(10) 2-Methyl-1-butanol, 3-methyl-1-butanol, and 2,2-dimethyl-1-butanol.

(11) 2-Propanol, 2-butanol, 2-pentanol, 2-hexanol, 2-octanol, 3-pentanol, 3-hexanol, 3-methyl-2-butanol, 3-methyl-2-pentanol, 4-methyl-2-pentanol, 3,3-dimethyl-2-butanol, cyclopentanol, and cyclohexanol.

(12) 2-Methyl-2-propanol, 2-methyl-2-butanol, and 2-methyl-3-pentanol.

total yield of 2 and 3 between this thiolate-containing complex base and  $\text{NaNH}_2\text{-NaO-}t\text{-Bu}$  (system 7) indicates that one-electron-transfer processes are unimportant.

Constancy in the relative proportions of 2 and 3 in reactions of 1 with complex bases that contain  $\text{NaNH}_2$  and a wide variety of sodium oxyanion (and other anionic) components strongly indicates that the latter function only to activate the surface of the elimination-inducing  $\text{NaNH}_2$ . Although the precise nature of this surface activation remains unclear, it is evident that for alkoxides a certain level of bulk is necessary. Thus, alkoxides derived from tertiary, secondary, and branched primary alcohols, but not those from *n*-alcohols, are effective complex-base components.

All the evidence that we have accumulated to date regarding the nature of complex-base-promoted syn eliminations is consistent with the transition-state structure represented in 4 in which B is the amide ion and M is the sodium cation.

**Registry No.** *trans*-1-Bromo-2-chlorocyclohexane, 13898-96-9; sodium amide, 7782-92-5; 15-crown-5, 33100-27-5.

**Supplementary Material Available:** Table II listing data for the elimination reactions of *trans*-1-bromo-2-chlorocyclohexane induced by  $\text{NaNH}_2\text{-Na(anion)}$  in THF at room temperature (1 page). Ordering information is given on any current masthead page.

## Notes

### Magnesium Anthracene Dianion

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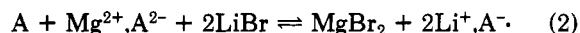
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In contrast to the black precipitate of magnesium which forms when magnesium bromide reacts with sodium naphthalene,<sup>1</sup> we have found that the corresponding reaction with sodium anthracene (deep blue) gives a white precipitate and a green-yellow solution. With lithium anthracene there is no visible reaction. It was also discovered that metallic magnesium reacts with anthracene in the presence of excess magnesium bromide to give rise to a green-yellow solution identical in color with that obtained from sodium anthracene. This solution has the curious property of reversibly changing color as the temperature is varied. At approximately 40 °C the solution is bright yellow, at 20 °C it is green-yellow, and as the temperature is lowered to -40 °C, the color smoothly changes to deep blue. Upon continued stirring of the reaction mixture at room temperature, an orange-yellow flocculent precipitate slowly formed. As no reports have yet appeared in the literature concerning the structure or physical properties of benzenoid aromatic radical anions or dianions which contain other than group 1A metals in ether solvents<sup>2</sup> and since the magnesium-anthracene complex was a solid, it was hoped that it could be crystallized for chemical and perhaps X-ray structure analysis. It quickly became obvious that the complex is only sparingly soluble in THF, and attempts to prepare the complex in DME or diethyl ether were unsuccessful. Conventional techniques of crystallization could not be used due to the low solubility and extreme air sensitivity of the complex.

Extraction of the orange-yellow precipitate over a period of 2 months in the DeKock-Streitwieser Soxhlet extractor<sup>3</sup> with THF gave large clear orange needles in a yellow solution. The material left on the frit of the extractor was a yellow-green solid, apparently insoluble in THF. This material was not examined further. The composition of the orange pyrophoric crystals was determined to be  $\text{MgA}\cdot 3\text{THF}$ , where A stands for anthracene. The analysis was achieved by EDTA titration for magnesium and gas chromatographic analysis for anthracene, with THF determined by weight difference. Since the value of three for the number of THFs of solvation is rather odd, the ratio of THF to anthracene was also determined by the relative integrations of THF to anthracene in the NMR spectrum of a carbon tetrachloride solution of a sample of the solid which had been treated with oxygen gas. As expected for an anthracene dianion, hydrolysis with water gave 9,10-dihydroanthracene with only 2% anthracene.<sup>4</sup> The small amount of anthracene was probably formed from adventitious oxygen.

X-ray single-crystal work on the  $\text{MgA}\cdot 3\text{THF}$  crystals proved to be quite difficult both from the standpoint of obtaining a suitable crystal free of twinning and analyzing the data. The method by which an untwinned crystal was finally obtained is described in the Experimental Section. It was determined that the unit cell was triclinic with a volume of 4668 Å<sup>3</sup>. The calculated density, assuming eight  $\text{MgA}\cdot 3\text{THF}$  units per unit cell, of 1.19 g/cm<sup>3</sup> is in excellent agreement with the experimental density of 1.18 g/cm<sup>3</sup>. Because of the very large size and lack of symmetry of the unit cell, plans for a structure determination were abandoned.

Returning to the interesting color changes described earlier, it would seem that a ready explanation is now available. This is illustrated in eq 1 and 2, where the first



equilibrium lies on the right at low temperatures and on

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