repeated three times, and the residue, after cooling, was extracted with CH_2Cl_2 and water. The porphyrin in the organic phase was purified by crystallization from CH_2Cl_2/MeOH: yield 51 mg (89%); NMR δ 1.98 (15 H, t, Et), 2.10 (6 H, t, Et), 4.16 (10 H, q, Et), 4.30 (4 H, q, Et), 9.16 (1 H, s, 8-H), 10.11, 10.16, 10.18, 10.20 (1 H each, s, meso); UV-vis λ_{max} (ϵ_M) 618.5 nm (9700), 565 (13000), 531.5 (16300), 498 (21000), 398.5 (215000); MS, found *m/e* 507.3457 for $(M + H)^+$, $C_{34}H_{43}N_4$ requires *m/e* 507.3491.

Reactions of *vic*-Dihydroxyetiochlorin I (7). Diol 7[5] was heated in dioxane/aqueous HCl in the same manner as described above. The overall yield for the two etioporphyrin alcohols was about 50%, with the ratio of 8 to 9 being near 2:1. If the diol 7 was heated in acetic acid, the acetoxy porphyrin 10 was obtained in 67% yield and 11 in 11% yield (6:1 ratio). These ratios can be observed directly by using NMR peaks of CH_2OR vs. CH(OR)Me: δ 6.10 (s, 8):6.52 (q, 9) = 4:1; 6.61 (s, 10):7.55 (q, 11) = 12:1.

Dimethyl 5-(Hydroxymethyl)-8-methyl-1,2,3,4-tetraethyl-6,7-porphinedipropionate (13). Diol 12[3] (40 mg) was heated in dioxane (10 mL)/aqueous HCl (10%, 4 mL) on a steam bath overnight. The solvent was evaporated, and the residue was esterified in $MeOH/H_2SO_4$. The principal product, isolated from TLC plates, was 13: 9.8 mg (~25% yield); NMR δ 1.90 (12 H, t, Et), 3.26 (4 H, t, $CH_2\mathit{CH_2}CO_2$), 3.49 (3 H, s, CH_3), 3.61, 3.66 (3 H each, s, CO_2Me), 4.05, 4.11 (8 H, q, Et), 4.42, 4.45 (2 H each, t, $\mathit{CH_2}CH_2CO_2$), 6.11 (2 H, s, CH_2OH), 10.06 (2 H, s, meso), 10.08, 10.28 (1 H each, s, meso), −3.78 (2 H, br s, NH); UV-vis λ_{max} 621.5 nm, 567, 535.5, 499.5, 402; MS, found *m/e* 639.3521 for $(M + H)^+$, $C_{38}H_{47}N_4O_5$ requires *m/e* 639.3549. The alternative alcohol 14 was not detected, but a small amount of acrylic porphyrin [~5% yield; NMR δ 7.05, 7.11, 9.28, 9.36, acrylic] was isolated, which can only result from 14.

Reactions of *vic*-Diols of Porphyrinones 15 and 17 (*Contributed by Weishih Wu*). Diol 15 was obtained by OsO_4 oxidation of 4-mesoporphyrinone dimethyl ester.[14] Like all other "southern" diols, 15 has a tendency to lactonize if left on silica gel; therefore, chromatography was carried out on a short column and as rapidly as possible: MS, found *m/e* 645.3299 for $(M + H)^+$, $C_{36}H_{45}N_4O_7$ requires *m/e* 645.3290; NMR δ 0.41 (3 H, t, 3-Et), 1.69 (3 H, t, 2-Et), 1.88 (3 H, d, 8-Me), 2.05 (3 H, s, 3-Me), 2.61 (2 H, m, 3-Et), 2.7–2.9 (4 H, m, 7-$CH_2CH_2CO_2$), 3.03, 4.05 (2 H each, q, 6-$CH_2CH_2CO_2$), 3.28, 3.34 (3 H each, s, 1- and 5-Me), 3.62, 3.65 (3 H each, s, OMe), 3.80 (2 H, q, 2-Et), 8.70, 8.85, 8.88, 9.52 (meso), −2.0 (NH); UV-vis λ_{max} 688 nm, 496, 413, 395. 15 was heated in a mixture of dioxane (6 mL), H_2O (3.5 mL), and concentrated HCl (0.5 mL) on a steam bath for 30 min. Since the resultant alcohol 16 was partially dehydrated, it was heated for further 10 min in the presence of concentrated H_2SO_4 (1 mL) to complete dehydration. The mixture was evaporated in a rotorvap as much as possible, and the residue was diluted in dry methanol (30 mL). After being allowed to overnight at room temperature, the solvent was evaporated and the acrylate ester product was purified by TLC (CH_2Cl_2): yield was about 85% from 15; NMR of the acrylate, δ 0.45 (3 H, t, Et saturated), 1.81 (3 H, t, Et), 2.06 (3 H, s, Me saturated), 2.76 (2 H, q, Et saturated), 3.23 (2 H, t, $CH_2\mathit{CH_2}CO_2$), 3.57, 3.58, 3.62 (3 H each, s, Me), 3.68 (3 H, s, propionate OMe), 3.99 (2 H, q, Et), 4.05 (3 H, s, acrylate OMe), 4.38 (2 H, t, $\mathit{CH_2}CH_2CO_2$), 6.98, 7.04 (1 H, dd, $=CHCO_2$), 9.12 (1 H, s, meso α), 9.19, 9.26 (1 H, dd, $\mathit{CH}=CHCO_2$), 9.80 (1 H, s, meso β), 9.87, 10.02 (1 H each, s, meso γ,δ), −2.89, −2.76 (1 H each, br s, NH); UV-vis λ_{max} 643 nm, 586, 567, 506, 415; MS, found *m/e* 609.3098 for $(M + H)^+$, $C_{36}H_{43}N_4O_6$ requires *m/e* 609.3079.

Diol 17 [NMR δ 1.88 (3 H, d, 5-Me), 2.22 (3 H, d, 1-Me), 8.79, 8.95, 8.91, 9.55 (meso); UV-vis λ_{max} 693 nm, 660, 633, 497, 414, 395], obtained from OsO_4 oxidation of 2-mesoporphyrinone dimethyl ester,[14] was heated in dioxane/aqueous HCl as described above. After esterification, the alcohol 18 was isolated from TLC plates: 78% yield; NMR δ 0.41 (3 H, t, Et saturated), 1.81 (3 H, t, Et), 2.06 (3 H, s, Me saturated), 2.76 (2 H, q, Et saturated), 3.29, 3.30 (2 H each, t, $CH_2\mathit{CH_2}CO_2$), 3.58, 3.67 (3 H each, s, Me), 3.68, 3.72 (3 H each, s, CO2Me), 4.04 (2 H, q, Et), 4.34, 4.40 (2 H each, t, $\mathit{CH_2}CH_2CO_2$), 5.78 (2 H, d, $\mathit{CH_2}OH$), 9.14 (1 H, s, meso δ), 9.83 (1 H, s, meso α), 9.95, 10.14 (1 H each, s, meso β,γ), −2.93 (2 H, br s, NH); UV-vis λ_{max} 640 nm, 582, 552, 512, 504, 410; MS, found *m/e* 627.3196 for $(M + H)^+$, $C_{36}H_{43}N_4O_6$ requires *m/e* 627.3184.

Acknowledgment. We thank Weishih Wu for results on the porphyrinones. This work was supported by NIH Grants GM36520 and GM 34468. C.K.C. is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Grant (1981–1986).

Kinetics and Mechanisms of Reactions of (Trialkylstannyl)lithiums with Chlorides Bearing Activating α Substituents

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Received August 14, 1986

In 1946 Whitmore and Sommer observed that (chloromethyl)trimethylsilane (1) (see Table I for structures) reacted somewhat more rapidly than did 1-chlorobutane with acetate, hydroxide, and ethoxide in protic solvents and with sodium iodide in dry acetone.[1] In contrast, they observed that 1 did not react with aqueous silver nitrate under conditions which led to ready reaction with 1-chlorohexane. Eaborn, in a series of studies,[2] examined the kinetics of the reaction of 1 with sodium iodide in acetone at 49.7 °C and found that its specific rate constant was 16 times that for 1-chlorobutane.[2a] The rate for (chloromethyl)trimethylstannane (2) was 360 times that for 1.[2c] Silylcarbinyl derivatives are generally less reactive than carbon analogues in solvolyses,[2d,3] but the reactivity can be reversed if the solvent is sufficiently nucleophilic.[3] These effects are consistent with theoretical treatments which show that an α-silyl group destabilizes a positive and stabilizes a negative charge on a carbinyl carbon.[3,4]

We have been conducting kinetic studies in connection with research on the mechanisms of reactions of organostannylalkalis with organic halides, eq 1. Such studies

$$RCHR'Cl + R''_3SnLi \rightarrow RCHR'CHSnR''_3 + LiCl \qquad (1)$$

should provide information concerning structure/reactivity relationships in nucleophilic substitutions involving nucleophiles with much greater reactivity than those which are normally studied. This reactivity can be maximized for reactions in solution because the dipolar aprotic solvents used have little capacity for solvating anions. It was of particular interest to obtain additional quantitative data concerning the activation by the silyl and stannyl groups and to compare these with other activating groups such as the phenyl and vinyl groups in benzylic and allylic derivatives, respectively. We also report on the enhanced reactivities of geminal and vicinal dichlorides as mechanistic indicators.

The products of the reactions studied were either known or were characterized by standard methods. Rates were measured in a stop–flow system which permitted reliable measurements of bimolecular rate constants in the range 10^{-1} to 10^3 M^{-1} s^{-1}. Pseudo-first-order conditions with excess halide were used and the rate constants were based on data covering more than 4 half-lives in all cases.

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Table I. Bimolecular Rate Constants for the Reaction of Equation 1[a]

		k_2 (M^{-1} s^{-1}) for reaction with	
entry	halide	Me_3SnLi	Vi_3SnLi
1	1-C_4H_9Cl	0.74	
2	2-C_4H_9Cl	ca. 10^{-3} [b]	
3	Me_3CCH_2Cl	ca. 10^{-5} [b]	
4	**1**, Me_3SiCH_2Cl	1015	3.03
5	**3**, $Me_3SiCHMeCl$	0.289	(9×10^{-4})
6	**4**, $(Me_3Si)_2CHCl$	186	
7	**2**, Me_3SnCH_2Cl	(1.4×10^5)	590
8	**5**, $Me_3SnCHMeCl$	101	0.436
9	$CH{=}CHCH_2Cl$	1790	7.84
10	$C_6H_5CH_2Cl$	1990	7.14
11	CH_2Cl_2	123[c]	
12	$MeCHCl_2$	24[c]	
13	Me_2CCl_2	7.1[c]	
14	$MeCHClCH_2Cl$	2.78	
15	$CH_2{=}CClCH_2Cl$	>3000	

[a] In tetrahydrofuran at 20 °C; stannyllithiums prepared by reaction of the distannanes with *n*-butyllithium at 0 °C. [b] Estimated from data using Me_3SnNa at 0 °C; see ref 11. [c] Statistically corrected.

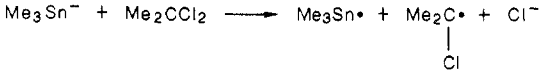
Correlation coefficients for individual runs were greater than 0.99. The values of k_2 showed standard deviatons of less than 10% in most cases; the largest were about 20%. These are small in comparison with the magnitude of the rate differences under consideration. Results are gathered in the table for reactions in tetrahydrofuran (THF) at 20 °C of chlorides with (trimethyl- and (trivinylstannyl)lithium. Inclusion of the latter provided a means of measuring the effect of the vinyl (Vi) group vs. that of methyl on the nucleophilicity of the stannyl anionoid and of extending the range of rates which could be estimated. The results show that Me_3SnLi was more reactive than Vi_3SnLi by factors ranging from 230 to 330, consistent with the relative inductive effects of the methyl and vinyl groups.

Comparison of entries 1 and 4 shows that Me_3SnLi reacts 1400 times as fast with **1** as with 1-chlorobutane. This ratio is much larger than the corresponding factor of 16 observed for iodide in acetone.[2a] The bimolecular rate constant for iodide with **1** at 20 °C is 2.2×10^{-5} M^{-1} s^{-1}.[2a] Hence the value for Me_3SnLi is 4.6×10^7 times that for the iodide, placing the stannyl anionoid in the supernucleophile category. It, therefore, replaces $LiEt_3BH$ (superhydride) as the most powerful simple nucleophile thus far available for S_N2 displacement reaction because the borohydride reacts only 2.5×10^3 times as fast as iodide.[5] Furthermore, the reactivity/selectivity principle does not apply when iodide and Me_3SnLi are compared.

Replacement of an α-hydrogen of **1** by methyl yields **3** which is less reactive than **1** by a factor of 3500 with Me_3SnLi. This steric effect is somewhat larger than the normal factor of about 100 for primary/secondary reactivity ratios,[7] revealing greater selectivity in this reaction. If one assumes that the effects of substitutions in the substrate have the same magnitude on reactivity for the reaction with Vi_3SnLi as with Me_3SnLi, one obtains the value in parentheses in entry 5. This value would not be accessible by direct measurement in our system. Introduction of a trimethylsilyl group (entry 6) in place of hydrogen in **1** as in **4** causes a decrease in rate by a factor of 5.5. This reveals that the steric effect of the second trimethylsilyl substituent outweighs any additional activating effect it may provide, but it still provides a substrate more reactive than 1-chlorobutane.

Compound **2** reacted with Me_3SnLi at a rate too fast to measure, but with Vi_3SnLi as the nucleophile the rate was measurable (entry 7). Introduction of an α-methyl group as in **5** lowered the rate of reaction with Me_3SnLi into the measurable range, and that with Vi_3SnLi could also be obtained. If one assumes that the **2**/**5** reactivity ratio for Me_3SnLi is the same as that for Vi_3SnLi, one obtains the value of 1.4×10^5 M^{-1} s^{-1} shown in parentheses in entry 7 for the reaction of **2** with Me_3SnLi. This apparently makes **2** the most reactive primary chloride thus far studied in the S_N2 reaction. The enhancement in reactivities of benzyl and allyl chlorides as compared with 1-chlorobutane is seen from entries 11 and 12 to approach 2000, comparable to that of **1**.

Activation toward S_N2 reactivity is observed due to certain electron-withdrawing groups such as acetyl, benzoyl, carbethoxy, and cyano.[6] This is generally attributed to conjugative delocalization of the negative charge in the transition state.[6] Other electron-withdrawing groups such as sulfonyl,[6] trifluoromethyl,[6] and halogens[7] have a marked deactivating effect. In the reaction with Me_3SnLi, the geminal dihalides show a significant acceleration relative to 1-chlorobutane as seen in entries 11–13. Also the effect of replacing each of the hydrogens of CH_2Cl_2 by methyls has a much smaller deactivating effect than is normally observed in S_N2 reactions. We have shown earlier that CCl_4 and $CHCl_3$ react with Me_3SnNa in THF by the halogen–metal exchange (HME) process by trapping of the anionic intermediates.[8] These kinetic results clearly indicate that the S_N2 mechanism is not operative here, but rather that some other mechanism such as electron transfer or halogen–metal exchange is involved. The latter was eliminated in the earlier work on the basis that $ClCH_2^-$ ions which would be the first intermediates were not trapped by reaction with alcohol as methyl chloride despite careful search for this product. Thus electron transfer seemed the remaining likely process. To test this we carried out the reaction of 2,2-dichloropropane with (trimethylstannyl)lithium in equimolar amounts and observed several products: 2-chloropropane, isoproprenyltrimethyltin, isopropyltrimethyltin, 2,2-bis(trimethylstannyl)propane, and hexamethylditin. However, when dicyclohexylphosphine, an efficient alkyl radical trap, was included in the reaction mixture, the yield of 2-chloropropane increased from 8.2% to 32%, and that of hexamethylditin increased from 52% to 84%. None of the other products were observed. This is clearly consistent with a free radical process in which the 2-chloropropyl radical is formed initially as in eq 2. Coupling of the trimethyltin radicals



$$Me_3Sn^- + Me_2CCl_2 \longrightarrow Me_3Sn\bullet + \underset{\displaystyle Cl}{\underset{|}{Me_2C\bullet}} + Cl^- \quad (2)$$

yields the hexamethylditin and hydrogen atom abstraction by the 2-chloro-2-propyl radical yields the 2-chloropropane. The additional products formed in the absence of the phosphine can be rationalized with these two radicals as precursors. In view of the reactivity pattern of the three vicinal dichlorides it seems reasonable to conclude that all react by the same mechanism. It is worth noting that after one chlorine of methylene chloride is replaced by a tri-

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methyltin group as in **2**, the remaining chlorine can be replaced by a second trimethyltin group about a thousand times as fast as the first. This accounts for the fact that **2** cannot be prepared from methylene chloride by reaction with 1 equiv of (trimethylstannyl)alkali.

It has been shown that vicinal dihalides react with Me_3SnNa to form alkenes by dehalogenation.[10] Kinetic studies were conducted to determine whether the elimination occurred primarily due to a strong driving force for the E_2 process or to large deactivation of the S_N2 process. The rate for 1,2-dichloropropane in entry 15 is four times greater than that for 1-chlorobutane, showing that the dominant driving force is enhancement of the formal abstraction of a halogen cation by the stannyl anion in the E_2 dehalogenation mechanism. This is also evident for 2,3-dichloropropene (entry 15) which reacted with Me_3SnLi at a rate too fast to measure. It was established that the only C_3 product was allene.

The foregoing results firmly establish the supernucleophilic behavior of silyl and stannyl anionoids.[12] They also reveal unexpectedly high selectivity toward typical organic chlorides, as well as the extremely high reactivity as S_N2 substrates of chlorides bearing a silyl or stannyl group on the carbinyl carbon. With these substrates, however, the selectivity is more nearly "normal" in that iodide reacts with **2** about 360 times as fast as with **1**; the corresponding factor is 140 for Me_3SnLi and 195 for Vi_3SnLi. Further study of the kinetics of these and other supernucleophiles with various substrates should contribute to our understanding of these and other structure/reactivity and reactivity/selectivity relationships.

Experimental Section

General. Halides were commercial samples if available or were prepared by standard methods. They were carefully distilled, checked for purity (>99%), and stored under argon before use. THF was dried and purified by distillation from calcium hydride and then from $LiAlH_4$ through a 12-in. packed column under argon. All reactions were conducted under argon using apparatus dried in the oven at 110 °C overnight. Reaction products were checked for identity by a comparison with authentic samples. NMR spectra were taken on a Varian EM360 instrument. GC/MS spectra were obtained with a Finnigan GC/MS data system series 9500/1015D/6000 using a $^1/_4$ in. × 8 ft stainless steel column packed with 10% SE-30 on Anakrom ABS.

The stopped flow system consisted of two pneumatically driven drive syringes, an eight-jet mixing chamber, and a 1-cm viewing cell of Kellef with quartz windows enclosed in a chamber through which water at 20 °C was circulated from a constant temperature bath. A Beckmann DU monochromator was used and a Dumont 1P28 photomultiplier tube (PMT) was used to collect transmitted light. The output was digitalized and collected by using a Kim-1 microcomputer. A General Radio 1191-Z counter was used to determine rates of data acquisition, which could range up to 6100 s^{-1}. The raw data could be viewed on an oscilloscope and processed on a mainframe computer (Univac 1110). Data were collected at 360 nm on the tail of the (organostannyl)lithium absorption band, thus permitting maximum initial concentrations of about 0.007 M to be viewed by the instrument. Concentrations of halide were always at least 10 times that of the organotinlithium, so pseudo-first-order kinetics were observed. At infinite time 100% trasmittance was observed in all experiments. Data were processed by the normal method and the Guggenheim method. Satisfactory agreement in the values of the rate constants were observed; if not, the data were not used. The reliability of the system was checked by using the reaction of tris(*o*-phenanthroline)ferrous sulfate with ceric sulfate in 0.5 M H_2SO_2 at 20 °C studied earlier by Sutin and Dulz.[13] Their rate constant at 25 °C, along with an activation energy of 6.50 kcal/mol, yielded a value of 1.18×10^{-5} M^{-1} s^{-1} at 20 °C compared with our measured value of 1.09 M^{-1} s^{-1}.

Preparation of (Trialkylstannyl)lithiums. A Schlenk tube filled with argon was charged with 1.88 mL of 1.65 M *n*-butyllithium (3.10 mmol) in hexane. The solvent was removed by evacuation with a vacuum pump, leaving a yellow oil. It was cooled to 0 °C and 6.0 mL of THF containing 3.11 mmol of hexamethylditin was added, yielding a pale yellow-green solution of (trimethylstannyl)lithium. This stock solution (0.45 M) was then diluted appropriately for charging the syringe of the stopped flow system which was done without exposure to air. (Trivinylstannyl)lithium was prepared in the same way from hexavinylditin.[14]

Reaction of 2,2-Dichloropropane with (Trimethylstannyl)lithium. A reaction between 0.38 M dichloride and 0.31 M (trimethylstannyl)lithium was conducted in THF at 0 °C. GC/MS analysis of the product mixture revealed peaks assigned to 2-chloropropane, isopropenyltrimethyltin, isopropyltrimethyltin, 2,3-bis(trimethylstannyl)propane, and hexamethylditin. When the same reaction was conducted in the presence of 1.6 M dicyclohexylphosphine, the yield of 2-chloropropane increased from 8.2% to 32%, that of hexamethylditin increased from 52% to 84%, and the yields of the other three products dropped to zero.

Acknowledgment. We are grateful for support of this work by the National Science Foundation (Grants CHE 810502101 and CHE 8318205) and for valuable advice concerning the design of the stop-flow system from Professor Y. P. Myer.

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Unusual β-Fluorination of Secondary Alkyl and Cycloalkyl Bromides in Their Reaction with $NO_2^+BF_4^-$ in $(HF)_n$-Pyridine Solution[1]

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Received September 9, 1986

Introduction

Halogen exchange fluorination of aliphatic halides is a widely used synthetic reaction.[2] The majority of cyclic halides, however, undergo elimination under the reaction conditions to give olefins. Recently Yoneda and coworkers[3] have reported halogen exchange fluorination of cyclic and acyclic halides without concommitant elimination by using cuprous oxide in anhydrous HF/THF (or ether) solution. In our continued investigation of the utility of the pyridinium polyhydrogen fluoride reagent,[4] we reported that bridgehead adamantyl and diamantyl halides undergo halogen exchange fluorination in the

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