an entry to ground-state triplet molecules.

Acknowledgment. This work was supported in part by AFOSR Grant No. 82-0114 and grants by the National Science Foundation.

Registry No. 1, 116076-59-6; 2, 116076-60-9.

Supplementary Material Available: Tables of bond lengths and bond angles (4 pages). Ordering information is given on any current masthead page.

Substituent Effects upon the Kinetics of Hydrogen Transfer from Triorganotin Hydrides to the 5-Hexen-1-yl Radical

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Received April 21, 1988

Steric and electronic substituent effects were probed for the hydrogen atom transfer reaction of a series of triorganotin hydrides with the 5-hexen-1-yl radical. Rate data were obtained for tributyltin hydride (**1**), triisopropyltin hydride (**2**), tri-*tert*-butyltin hydride (**3**), trineopentyltin hydride (**4**), trimesityltin hydride (**5**), and dibutylethoxytin hydride (**6**). Arrhenius parameters are reported for the reactions of **1**–**4** and **6**; the reaction of **5** was studied only at 50 °C. For compounds **1**–**4**, the activation energy, E_a, decreased monotonically with increasing alkyl size from 3.9 ± 0.1 to 3.1 ± 0.1 kcal mol^{-1}. The preexponential factor, expressed as log A, decreased monotonically from 9.4 ± 0.1 to 8.8 ± 0.1. The effect of the ethoxy substituent, **6**, relative to an n-butyl substituent, **1**, upon the activation energy was negligible (4.2 ± 0.2 versus 3.9 ± 0.1 kcal mol^{-1}, respectively), but the preexponential factor, log A, increased from 9.4 ± 0.1 to 10.0 ± 0.1. The activation data for **1**–**4** are interpreted in terms of the steric requirements of the alkyl groups appended to tin. The lack of a significant substituent effect upon E_a by the ethoxy group is reflective of a nonpolarized transition state for the hydrogen atom transfer reaction.

Introduction

Since Ingold and co-workers[1] reported the Arrhenius parameters for the cyclization of the 5-hexen-1-yl radical, the rearrangement has been useful as a "clock" for reactions involving free radical intermediates.[2] The reduction reaction of 6-halo-1-hexene is particularly well suited for the kinetic study of the hydrogen atom transfer from a metal hydride to a carbon-centered free radical. This has been demonstrated by Ingold and co-workers for the determination of the rate of hydrogen abstraction from tributylgermanium hydride.[3] Reactions 1–4 pertain to a generalized application of the method under free radical chain conditions. When the initial concentration of the metal hydride greatly exceeds that of the 5-hexen-1-yl substrate, the value of K_H is given by eq 5.[3]

$$M^\bullet + CH_2{=}CHCH_2CH_2CH_2CH_2X \xrightarrow{k_x} MX + CH_2{=}CHCH_2CH_2CH_2CH_2^\bullet \quad (1)$$

$$CH_2{=}CHCH_2CH_2CH_2CH_2^\bullet + M{-}H \xrightarrow{k_H} CH_2{=}CHCH_2CH_2CH_3 + M^\bullet \quad (2)$$

$$CH_2{=}CHCH_2CH_2CH_2CH_2^\bullet \xrightarrow{k_c} c\text{-}C_5H_9CH_2^\bullet \quad (3)$$

$$c\text{-}C_5H_9CH_2 + M{-}H \xrightarrow{k_H'} c\text{-}C_5H_9CH_3 + M^\bullet \quad (4)$$

$$k_H = \frac{k_c}{[M{-}H]_0}\,\frac{[\text{1-hexene}]}{[\text{methylcyclopentane}]} \quad (5)$$

Table I. Reaction of *n*-Undecyl Iodide with Triorganotin Hydrides[a]

hydride	recovered n-$C_{11}H_{23}I$,[b] %	yield n-$C_{11}H_{24}$,[b] %
1	4	98
2	<1	97
3	<1	98
4	2	95
5	11	91
6	<1	98

[a] Triorganotin hydride (0.100 mmol), 1-iodoundecane (0.100 mmol) and AIBN (0.01 mmol) in 5 mL of benzene, refluxed 8 h under a nitrogen atmosphere. [b] Determined by GLC with n-dodecane as an added integration standard. Precision is ca. ±3%.

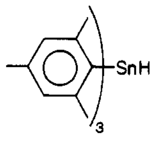
We have evaluated the kinetic parameters for the abstraction of hydrogen atom by 5-hexen-1-yl by triorganotin hydrides **1**–**6**. The kinetic parameters for **1** have been previously determined by Ingold.[1a,4] Compounds **2**–**6** have not been previously studied in this regard. Compounds **1**–**4** and, arguably, **5**, differ primarily in the steric requirements of the organic ligands appended to tin. Compound **6** bears an alkoxy ligand, which exerts a significantly different electronic effect than do alkyl ligands.

$(CH_3CH_2CH_2CH_2)_3SnH$ **1**

$[(CH_3)_2CH]_3SnH$ **2**

$[(CH_3)_3C]_3SnH$ **3**

$[(CH_3)_3CCH_2]_3SnH$ **4**



5

$(CH_3CH_2CH_2CH_2)_2(CH_3CH_2O)SnH$ **6**

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[4] The actual rate measurement was for the reaction of ethyl radical with tri-*n*-butyltin hydride. This was taken by the authors of ref 1a as equivalent to rate of 5-hexen-1-yl with the hydride. This information, in turn, was used to calcualte the activation parameters for the 5-hexen-1-yl cyclization.

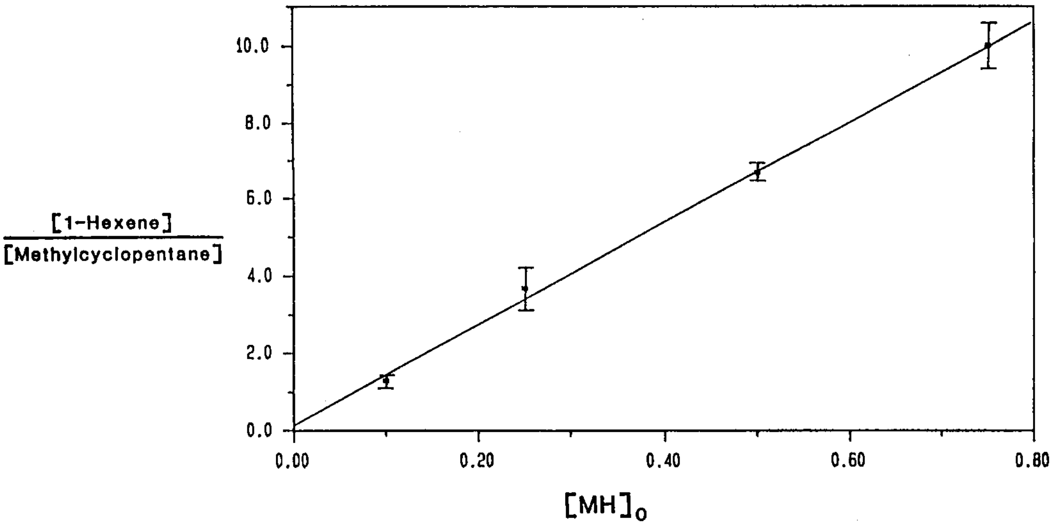

Figure 1. Plot of the product ratio (1-hexene/methylcyclopentane) versus the initial concentration of the metal hydride (mol L^{-1}). Equation 9 predicts a zero intercept and a slope equal to k_H/k_c. The line is the weighted linear least-squares fit. The error bars represent one standard deviation in the determination of the product ratio.

Results and Discussion

The metal hydrides employed in this study were each tested for their behavior toward a simple alkyl halide, 1-iodoundecane (reaction 6). Table I verifies that com-

$$R_3MH + n\text{-}C_{11}H_{23}I \xrightarrow[\text{benzene}\atop\text{reflux}]{\text{AIBN}} R_3MI + n\text{-}C_{11}H_{24} \qquad (6)$$

pounds **1**–**6** are all capable of reducing an alkyl halide under free radical chain conditions. These reactions were performed in refluxing benzene with 10 mol % AIBN added as a free radical initiator. In all cases the sum of the yields of hydrocarbon product and the recovered iodide was 100 ± 2%. The reaction of **5**, trimesityltin hydride, was sluggish. Whether it would react at all was originally an open question: the germanium analogue of **5**, trimesitylgermanium hydride, is completely unreactive toward 1-iodoundecane.[5]

Reaction 7 was performed with a tenfold excess of the metal hydride. When rigorous degassing procedures were

$$CH_2{=}CHCH_2CH_2CH_2CH_2Br + R_3SnH \xrightarrow[\mathbf{1\text{–}6}]{\text{dodecane}}$$
$$CH_2{=}CHCH_2CH_2CHCH_3 + c\text{-}C_5H_9CH_3 + R_3SnBr \qquad (7)$$

observed (see the experimental section), all of the tin hydrides reacted spontaneously with 6-bromo-1-hexene without the addition of initiators such as AIBN. We observed the practice of permitting an alkenyl bromide conversion of only 50% or less in reaction 7.[3] This was necessary to prevent the free radical hydrostannylation of the 1-hexene (reaction 8) which readily occurs when 6-

$$M{-}H + CH_2{=}CHCH_2CH_2CH_2CH_3 \rightarrow$$
$$M{-}CH_2CH_2CH_2CH_2CH_2CH_3 \qquad (8)$$

bromo-1-hexene is not available to intercept triorganotin radicals via reaction 2.[6] Conversions of 6-bromo-1-hexene between 20% and 50% were optimal. The length of time required to obtain the desired extent of reaction varied widely according to the identity of the triorgantin hydride and the reaction temperature. The shortest reaction times were ca. 15 min; the longest were ca. 24 h.

Since reaction mixtures had to be analyzed prior to completion, it was necessary to ensure that a reaction did not continue during the product analysis and that the product ratio was not influenced by reaction on the heated injection port of the gas chromatograph. Consequently, each reaction mixture was quenched by cooling in an ice bath followed by the addition of a large excess of 1-iodoundecane (200% relative to the tin hydride). Control experiments verified that the alkyl iodide was far more reactive than 6-bromo-1-hexene toward the metal hydride.

The selected concentrations of metal hydride were 0.50 or 0.25 M. It was assumed that these rather high concentrations are equivalent to the thermodynamic activities. This supposition is supported by Figure 1. Equation 9, obtained by rearrangement of eq 5, predicts a linear relationship between the hydrocarbon product ratio [1-hexene]/[methylcyclopentane], and the metal hydride concentration. The reaction of triisopropyltin hydride (**2**)

$$\frac{[\text{1-hexene}]}{[\text{methylcyclopentane}]} = \frac{k_H}{k_c}[M{-}H]_0 \qquad (9)$$

was evaluated at 15 C for 0.10 M ≤ $[M{-}H]_0$ ≤ 0.75 M. The least-squares line in Figure 1 gives almost precisely the predicted zero y intercept.

The data required for the derivation of Arrhenius parameters are given in Table II. A minimum of five temperatures over a minimum temperature span of 50 K were evaluated for each hydride. The actual temperatures were selected according to the qualitative reactivity of a given tin hydride toward 6-bromo-1-hexene. This was determined by trial and error. The primary trialkyltin hydrides **1** and **4** reacted more sluggishly than the secondary and tertiary trialkyltin hydrides **2** and **3** or the di-*n*-butyl ethoxytin hydride (**6**). This appears to be a general trend for the rate of self-initiation of the reaction between organic halides and triorganotin hydrides.[5]

Compound **3** was particularly labile toward reaction with 6-bromo-1-hexene. In order to employ the desired temperature range, it was necessary to perform reaction 7 at 253 K, several degrees below the freezing point of *n*-dodecane. *n*-Decane was employed as the solvent at this temperature. The applicability of data in this solvent was verified by the use of *n*-decane at 273 K; data from the

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Table II. Kinetic Data for the Reaction of Triorganotin Hydrides with the 5-Hexen-1-yl Radical

tin hydride	T,[a] K	R[b]	$10^{-6}k_H$,[b] M^{-1}/s^{-1}
1[c]	338	0.302 ± 0.027	6.6 ± 0.6
1[c]	323	0.255 ± 0.021	4.9 ± 0.4
1[c]	308	0.194 ± 0.016	3.8 ± 0.3
1[c]	293	0.154 ± 0.009	2.7 ± 0.2
1[c]	273	0.108 ± 0.008	1.6 ± 0.1
2[c]	323	0.274 ± 0.010	4.4 ± 0.2
2[c]	313	0.245 ± 0.008	3.6 ± 0.2
2[c]	298	0.195 ± 0.007	2.6 ± 0.1
2[c]	288	0.150 ± 0.003	2.3 ± 0.1
2[c]	273	0.129 ± 0.012	1.4 ± 0.1
3[d]	313	0.628 ± 0.030	2.9 ± 0.1
3,[d]	298	0.444 ± 0.037	2.3 ± 0.2
3[d]	288	0.457 ± 0.066	1.5 ± 0.2
3[d]	273	0.296 ± 0.030	1.2 ± 0.1
3[d]	263	0.231 ± 0.017	0.95 ± 0.07
3[d]	253[e]	0.173 ± 0.009	0.75 ± 0.04
4[d]	338	0.627 ± 0.018	6.4 ± 0.3
4[d]	323	0.520 ± 0.037	4.8 ± 0.3
4[d]	308	0.385 ± 0.014	3.8 ± 0.2
4[d]	293	0.289 ± 0.005	2.89 ± 0.04
4[d]	273	0.175 ± 0.001	2.03 ± 0.03
6[d]	348	0.229 ± 0.011	23 ± 1
6[d]	328	0.205 ± 0.011	14 ± 1
6[d]	313	0.158 ± 0.016	11 ± 1
6[d]	298	0.122 ± 0.010	8.4 ± 0.6
6[d]	273	0.0844 ± 0.0053	4.2 ± 0.3

[a] Absolute temperatures are controlled within ±0.1 K. [b] R = (yield of methycyclopentane)/(yield of 1-hexene). The uncertainty interval is one standard deviation based on a minimum of three trials. [c] [Hydride] = 0.50 M. [d] [Hydride] = 0.25 M. [e] To avoid freezing of the solvent, *n*-decane was substituted for *n*-dodecane.

Table III. Arrhenius Parameters for the Reaction of the 5-Hexen-1-yl Radical with Triorganotin Hydrides

hydride	E_a,[a] kcal mol^{-1}	log A[a]	k_H(50 °C),[b] M^{-1} s^{-1}
1	3.9 ± 0.1	9.4 ± 0.1	5.0×10^6
1	3.7 ± 0.3[c]	9.1 ± 0.2[c]	3.8×10^6 [c]
2	3.6 ± 0.3	9.1 ± 0.2	4.4×10^6
3	3.5 ± 0.2	8.9 ± 0.1	3.4×10^6
4	3.1 ± 0.1	8.8 ± 0.1	4.8×10^6
5	...	...	$>1.1 \times 10^7$
6	4.2 ± 0.2	10.0 ± 0.1	1.4×10^7

[a] Arrhenius parameters according to eq 10 calculated from the data in Table II. The uncertainty corresponds to one standard deviation derived from the weighted linear regression analysis of log k versus $1/T$. [b] Calculated from the Arrhenius equation. [c] Data taken from Ingold[3] for comparison. [d] The only value of k_H experimentally determined was at 50 °C (see text).

reaction in *n*-decane and *n*-dodecane were indistinguishable.

The reaction of 6, trimesityltin hydride, was only studied at 323 K owing to the low solubility of this high-melting crystalline hydride. In fact, the solubility in *n*-dodecane was sufficiently low to require the introduction of naphthalene as a cosolvent (see the Experimental Section). Under these conditions, the ratio of 1-hexene to methylcyclopentane was too large to accurately measure. Thus, only a limiting value for k_H is reported in Table II.

The Arrhenius parameters for the k_H process for hydrides 1–4 and 6 are given in Table III. They pertain to the form of the Arrhenius expression shown in eq 10.

$$k_H = Ae^{-E_a/RT} \qquad (10)$$

Table III compares the activation parameters for tri-*n*-butyltin hydride (1) obtained by us with those reported by Ingold et al.[1a,4] The results are identical within experimental error, verifying the compatibility of our techniques with those of other workers. As a further self-check, we determined k_H for tri-*n*-butylgermanium hydride at 50 °C (not shown in Table II or Table III) and obtained 1.8×10^5 M^{-1} s^{-1} identical with the value obtained from Ingold's activation parameters for this reaction.[3]

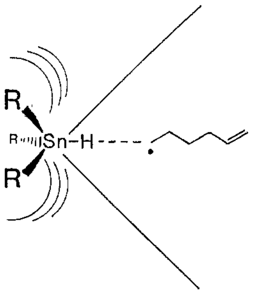
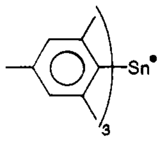


Figure 2. Pictoral representation of an encounter between a triorganotin hydride and a 5-hexen-1-yl radical. The steric requirements of the R groups appended to the tin atom influence the angular requirement for a productive encounter trajectory. Variations in the steric size of R are reflected in the magnitude of the Arrhenius preexponential factor.

Variations in the reactivity of metal hydrides **1**, **2**, **3**, **4**, and **5** are best interpreted as relating to the varying steric requirements of the organic ligands appended to tin. Exercises with space-filling models suggested to us that the trineopentyltin hydride (**4**) might be sufficiently sterically congested to impede the approach of the 5-hexen-1-yl radical (Figure 2). If this occurred, an exalted value of E_a would result. Clearly, a trajectory for the approach of the 5-hexen-1-yl radical free of steric interference is available for hydrides 1–4. Indeed, the value of E_a decreases monotonically with increasing steric bulk of the alkyl ligands from 3.9 ± 0.1 kcal mol^{-1} for 1 to 3.1 ± 0.1 kcal mol^{-1} for 4. One interpretation of these data is that E_a is responsive to steric repulsion between the alkyl ligands; this steric repulsion is relieved by abstraction of a hydrogen atom and formation of a resultant trialkyltin radical. Such radicals are believed to be intermediate in struture between trigonal planar (sp^2 hybridization on tin) and tetrahedral (sp^3),[7] whereas triorganotin hydrides have C–Sn–C and C–Sn–H bond angles corresponding to nearly perfect tetrahedra.[8]

The value of the Arrhenius preexponential factor, expressed as log A, decreases monotonically with increasing steric bulk of the alkyl ligands. This trend can be understood in terms of the increasing geometrical requirements for a successful collisional encounter between the 5-hexen-1-yl radical and tin hydride with increasing alkyl ligand size (Figure 2).

The value of k_H at 50 °C for 5 suggests that there is no appreciable steric hindrance restricting the approach of the 5-hexen-1-yl radical to the hydridic hydrogen of trimesityltin hydride. This is interesting in light of the known persistence of 7 due, presumably, to the steric barrier to dimerization.[9]



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The ethoxy group on tin in compound **6** is potentially capable of exerting an electronic substituent effect. Relative to an alkyl group, an alkoxy group is electron-withdrawing. This is shown by the increased Lewis acidity of organotin compounds bearing oxy substituents compared to carbon substituents.[10] The activation energy for **6** (see Table III) is, within one standard deviation, the same as that for tri-*n*-butyltin hydride (**1**). We interpret this as an indication that the transition state for hydrogen atom transfer is not extensively polarized. The preexponential factor for **6**, log A, is 10.0 ± 0.1 versus 9.4 ± 0.1 for tri-*n*-butyltin hydride (**1**). Presumably, this reflects the smaller size of the ethoxy ligand relative to *n*-butyl.

In conclusion, alkyl ligands on tin ranging in size from *n*-butyl to neopentyl exert a small but measurable effect upon the Arrhenius parameters for the abstraction of hydrogen from a trialkyltin hydride by the 5-hexen-1-yl radical. The activation barrier, E_a, decreases as the steric bulk of the alkyl ligands increases. Likewise, the preexponential factor diminishes with increasing alkyl size. A kinetic study of the hydrogen transfer process for trimesityltin hydride at 50 °C showed no evidence for any special substituent effect for the bulky mesityl group. The lack of a substantial electronic substituent effect for the ethoxy substituent in di-*n*-butylethoxytin hydride reflects the nonpolarized nature of the transition state for the hydrogen atom transfer process.

Experimental Section

Materials. The solvents, *n*-dodecane and *n*-decane, were purchased from Aldrich, vacuum-distilled, and stored in glass under nitrogen. The 1-iodoundecane and 6-bromo-1-hexene were used as received from Aldrich. Triisopropyltin hydride (**2**),[11-16] tri-*tert*-butyltin hydride (**3**),[11,17,18] trineopentyltin hydride (**4**),[11,19,21] trimesityltin hydride (**5**),[7,9] and di-*n*-butylethoxytin hydride (**6**)[22,23] were prepared according to literature methods. Tri-*n*-butyltin hydride (**1**) was prepared by the reaction of ethereal lithium aluminum hydride with tri-*n*-butyltin chloride. Hydrides **1**–**4** and **6** were carefully vacuum distilled and stored in vacuum-sealed ampules at −5 °C. Hydride **5**, a crystalline material (mp 168–169 °C (lit.[7] mp 168 °C)), was stored under argon. In our hands, these hydrides could be stored for several days without detectable change. A notable exception is compound **3**, tri-*tert*-butyltin hydride, which reacted rather sluggishly with 6-bromo-1-hexene if stored more than 2 or 3 days. All of the liquid metal hydrides were >98% pure by GLC and afforded appropriate ^{1}H NMR and IR spectra.

Instrumentation. Gas chromatography was performed on a Shimadzu GC-8A equipped with a Shimadzu C-R3 Chromatopac integrator. The column was a 30-m SE-30 fused silica capillary.

Reactions of 1, 2, 3, 4 and 6 with 6-Bromo-1-hexene. An 18-in. sealable Pyrex tube was flushed with argon and chilled in an ice bath. The solvent (usually dodecane), the metal hydride, and the 6-bromo-1-hexene were transferred to the bottom of the tube by using a syringe with a long needle. The solution volume was 2 mL. The hydride concentration was usually 0.25 or 0.50 M, according to Table II. The 6-bromo-1-hexene concentration was one-tenth that of the hydride. The tube was cooled in liquid nitrogen and evacuated. For experiments using hydride **1**, **2**, **4**, and **6**, the contents of the tube were degassed by three freeze–thaw cycles. The tube was then vacuum-sealed at liquid nitrogen temperature. Hydride **3** was prone to spontaneous reaction with the alkenyl bromide during the freeze–thaw procedure; tubes containing **3** were cooled in liquid nitrogen immediately after the initial mixing and sealed under vacuum. For each rate constant evaluation at a given temperature, four identical tubes were prepared: three for reaction and one as a reference to verify that reaction had not occurred during the preparation of the reaction mixture. The three reaction tubes were placed in the constant-temperature bath for a length of time sufficient for reduction of between 20% and 50% of the 6-bromo-1-hexene (this time must be determined by trial and error). Typical reaction times range from 25 min to 24 h. The reaction tubes were then quenched by immersion in liquid nitrogen followed by scoring, opening, and addition of 1-iodoundecane (200% molar excess based upon tin). Benzene was added as an integration standard, and the relative and absolute yields of 1-hexene and methylcyclopentane were determined as the average of at least three GLC injections per reaction tube. The reference tube, instead of being subjected to the reaction conditions of the constant temperature bath, was kept in liquid nitrogen until it was opened and quenched with 1-iodoundecane along with three reaction tubes. GLC analysis of the reference tube invariable showed that no reduction of 6-bromo-1-hexene had occurred.

Reaction of 5 with 6-Bromo-1-hexene. Trimesityltin hydride was found to be nearly insoluble in dodecane. This reaction was performed at 50 °C in a 0.75:1.00 (w/w) mixture of dodecane and naphthalene. The concentrations of **6** and 6-bromo-1-hexene were 0.50 and 0.050 M, respectively. The ratio of 1-hexene: methylcyclopentane produced by the reaction was too high (>20:1) to accurately determine by GLC. Thus, the value of k_H in Table III is reported only as a lower limit.

Acknowledgment. We thank the Miami University Faculty Research Committee and the Miami University Undergraduate Research Program (grant to M.R.) for financial support.

Registry No. **1**, 688-73-3; **2**, 759-23-9; **3**, 16216-29-8; **4**, 52741-72-7; **5**, 56797-46-7; **6**, 16524-93-9; *n*-undecyl iodide, 4282-44-4; 5-hexen-1-yl radical, 16183-00-9.

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